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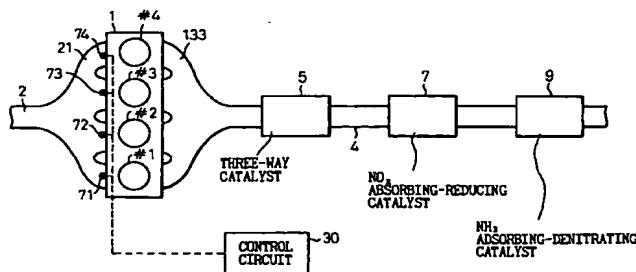
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(54) An exhaust gas purification device for an internal combustion engine

(57) In an exhaust gas purification device, a three-way catalyst, an NO_x absorbing-reducing catalyst and an NH₃ adsorbing-denitrating catalyst are disposed in an exhaust gas passage of the internal combustion engine. The engine is provided with direct cylinder injection valves which inject fuel directly into the respective cylinders. A control circuit controls the amount of fuel injected from the injection valve so that the air-fuel ratio of the combustion in the cylinders becomes a lean air-fuel ratio during the normal operation of the engine. Therefore, a lean air-fuel ratio exhaust gas is discharged from the cylinders during the normal operation and NO_x in the exhaust gas is absorbed by the NO_x absorbing-reducing catalyst. When the amount of NO_x

absorbed in the NO_x absorbing-reducing catalyst increases to a predetermined level, the control circuit performs an additional fuel injection during the expansion stroke or exhaust stroke of cylinders in order to adjust the air-fuel ratio of the exhaust gas leaving the cylinders to a rich air-fuel ratio. The rich air-fuel ratio exhaust gas leaving the cylinders flows into the three-way catalyst and NO_x in the exhaust gas is converted into NH₃ at the three-way catalyst. When the rich air-fuel ratio exhaust gas flows through the NO_x absorbing-reducing catalyst, NO_x is released from the NO_x absorbing-reducing catalyst and is reduced to N₂ by NH₃ in the exhaust gas.

Fig.1



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Description

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to an exhaust gas purification device for an internal combustion engine. More specifically, the invention relates to a device which is capable of removing NO_x from the exhaust gas of a lean burn engine with high efficiency.

10 2. Description of the Related Art

An exhaust gas purification device utilizing a three-way reducing and oxidizing catalyst (hereinafter referred to as a "three-way catalyst") is commonly used for removing HC, CO and NO_x from the exhaust gas of an internal combustion engine (in this specification, the term NO_x means a nitrogen oxide such as NO, NO_2 , N_2O and N_2O_4 , in general). The three-way catalyst is capable of oxidizing HC and CO, and reducing NO_x in the exhaust gas when the exhaust gas is at a stoichiometric air-fuel ratio. Namely, the three-way catalyst is capable of simultaneously removing these harmful compounds from exhaust gas when the air-fuel ratio of the exhaust gas is the stoichiometric air-fuel ratio.

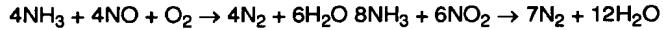
However, the ability of the three-way catalyst for reducing NO_x becomes lower as the air-fuel ratio of the exhaust gas becomes leaner (i.e., as the air-fuel ratio becomes higher than the stoichiometric air-fuel ratio). Therefore, it is difficult to remove NO_x in the exhaust gas from a lean burn engine, which is operated, on the whole, at a lean air-fuel ratio, using a three-way catalyst.

To solve this problem, Japanese Unexamined Patent Publication (Kokai) No. 4-365920 discloses an exhaust gas purification device utilizing a denitrating reaction.

25 When the air-fuel ratio of the exhaust gas is lower than the stoichiometric air-fuel ratio (i.e., when the air-fuel ratio of the exhaust gas is rich), the three-way catalyst converts a portion of NO_x in the exhaust gas to NH_3 while reducing most of NO_x in the exhaust gas and converting it into N_2 . The device in the '920 publication produces NH_3 from NO_x in the exhaust gas using a three-way catalyst, and reacts the produced NH_3 with the NO_x in the exhaust gas to reduce NO_x to N_2 and H_2O by a denitrating reaction.

30 In the '920 publication, a multi-cylinder internal combustion engine is used, and a group of cylinders of the engine are operated at a rich air-fuel ratio while other cylinders are operated at a lean air-fuel ratio, and the operating air-fuel ratio of the engine, as a whole, is kept at a lean air-fuel ratio. Further, a three-way catalyst having a high capability for converting NO_x to NH_3 is disposed in an exhaust gas passage connected to the rich air-fuel ratio cylinders (i.e., the cylinders operated at a rich air-fuel ratio). After it flows through the three-way catalyst, the exhaust gas from the rich air-fuel ratio cylinders mixes with the exhaust gas from the lean air-fuel ratio cylinders. When the exhaust gas from the rich air-fuel ratio cylinders flows through the three-way catalyst, a portion of the NO_x in the exhaust gas is converted to NH_3 . Thus, the exhaust gas downstream of the three-way catalyst contains a relatively large amount of NH_3 . On the other hand, the exhaust gas from the lean air-fuel ratio cylinders contains a relatively large amount of NO_x . Therefore, by mixing the exhaust gas from the three-way catalyst and the exhaust gas from the lean air-fuel ratio cylinders, NH_3 in the exhaust gas from the three-way catalyst reacts with NO_x in the exhaust gas from the lean air-fuel ratio cylinder, and NH_3 and NO_x produce N_2 and H_2O by a denitrating reaction. Thus, according to the device in the '920 publication, NO_x is removed from the exhaust gas.

35 In the device of the '920 publication, it is required that the amount of NH_3 produced by the three-way catalyst is sufficient for reducing all of the NO_x in the exhaust gas from the lean air-fuel ratio cylinders. For example, the greatest part of NO_x in the exhaust gas discharged from the engine is composed of NO (nitrogen monoxide) and NO_2 (nitrogen dioxide) components. These NO and NO_2 components react with NH_3 and produce N_2 and H_2O by the following denitrating reactions.



40 Therefore, in the device of the '920 publication, an amount of NH_3 which equals the total of the number of moles of NO and $4/3$ times the number of moles of NO_2 is required in order to remove all of the NO_x in the exhaust gas from the lean air-fuel ratio cylinders. When the exhaust gas contains other NO_x components such as N_2O_4 , N_2O , the amount of NH_3 stoichiometrical to the amount of these components is required in addition to the above noted amount on NH_3 .

45 55 However, the amount of NO_x produced in the cylinders of the engine becomes the maximum when the cylinders are operated at a lean air-fuel ratio (for example, at an excess air ratio about 1.2), and decreases rapidly when the cylinders are operated at a rich air-fuel ratio. Since the device in the '920 publication converts NO_x in the exhaust gas of the rich air-fuel ratio cylinder to produce NH_3 , the amount of produced NH_3 is limited by the amount of NO_x produced

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in the rich air-fuel ratio cylinders. Therefore, in the device of the '920 publication, the amount of NH_3 produced by the three-way catalyst is not sufficient to reduce all of the NO_x in the exhaust gas from the lean air-fuel ratio cylinders, and a part of NO_x in the exhaust gas from the lean air-fuel ratio cylinder is released to the atmosphere without being reduced.

5 Further, in the device of the '920 publication, a group of the cylinders are operated at a lean air-fuel ratio, while other cylinders of the engine is operated at a rich air-fuel ratio. This causes a difference in the output torque of the cylinders, and causes fluctuations in the output torque of the engine.

SUMMARY OF THE INVENTION

10 In view of the problems in the related art as set forth above, the object of the present invention is to provide an exhaust gas purification device for an internal combustion engine which is capable of removing NO_x in the exhaust gas of a lean burn engine, with high efficiency, by producing a sufficient amount of NH_3 and removing NO_x from the exhaust gas by reacting the produced NH_3 and NO_x in the exhaust gas and without causing fluctuations in the output torque of the engine.

15 This object is achieved by an exhaust gas purification device for an internal combustion engine according to the present invention in which the engine is provided with a direct cylinder injection valve for injecting fuel directly into the cylinder thereof and is capable of operating on a lean air-fuel ratio combustion in the cylinder. The exhaust gas purification device comprises exhaust gas air-fuel ratio adjusting means for adjusting the air-fuel ratio of the lean air-fuel ratio 20 exhaust gas produced by the lean air-fuel ratio combustion in the cylinder to a rich air-fuel ratio by injecting fuel into the cylinder from the direct cylinder injection valve during an expansion stroke or an exhaust stroke of the cylinder, NH_3 conversion means disposed in an exhaust gas passage through which the exhaust gas after its air-fuel ratio is adjusted flows and for producing NH_3 by converting at least a part of NO_x contained in the exhaust gas to NH_3 and purification means disposed in an exhaust gas passage into which the exhaust gas from the NH_3 conversion means flows and for 25 purifying both NO_x and NH_3 in the exhaust gas by reacting NO_x with NH_3 in the exhaust gas.

30 In the present invention, the combustion in the cylinder of the engine is performed at a lean air-fuel ratio. Therefore, the amount of NO_x produced by the combustion in the cylinder is larger than the amount of the same when the cylinder is operated at a rich air-fuel ratio. Thus, exhaust gas with a lean air-fuel ratio and containing a relatively large amount of NO_x is formed in the cylinder. The exhaust gas air-fuel ratio adjusting means adds fuel to this lean air-fuel ratio 35 exhaust gas by injecting fuel into cylinder during the expansion stroke or the exhaust stroke using the direct cylinder injection valve. Since fuel is added to the exhaust gas, the air-fuel ratio of the exhaust gas changes to a rich air-fuel ratio. Further, since the amount of NO_x produced by the lean air-fuel ratio combustion does not change by the fuel injection during the expansion or the exhaust stroke, the exhaust gas still contains a relatively large amount of NO_x even after the fuel injection during the expansion or the exhaust stroke is performed. Thus, exhaust gas with a rich air-fuel ratio which contains a relatively large amount of NO_x is formed in the cylinder by the direct cylinder fuel injection during the expansion or the exhaust stroke. It will be understood that the amount of NO_x contained in this rich air-fuel ratio 40 exhaust gas is larger than the amount of NO_x contained in the exhaust gas formed by a rich air-fuel ratio combustion.

45 This exhaust gas, having a rich air-fuel ratio and containing a relatively large amount of NO_x , is supplied to the NH_3 conversion means such as a three-way catalyst or a NO_x absorbing-reducing catalyst. Since the amount of NO_x in the exhaust gas is large, a large amount of NH_3 is produced by the NH_3 conversion means and is supplied to the purification means. Therefore, a sufficient amount of NH_3 for reducing NO_x in the exhaust gas is supplied to the purification means.

Further, since the fuel injected into the cylinder during the expansion stroke or the exhaust stroke does not generate output torque at the cylinder, the engine output torque is not affected by the fuel injection during the expansion 45 stroke or the exhaust stroke. Therefore, according to the present invention, NO_x in the exhaust gas is purified with high efficiency without causing fluctuations in the output torque of the engine.

BRIEF DESCRIPTION OF THE DRAWINGS

50 The present invention will be better understood from the description as set forth hereinafter, with reference to the accompanying drawings in which:

Fig. 1 schematically illustrates the general configuration of an embodiment of the exhaust gas purification device according to the present invention;
 55 Fig. 2 is a sectional view of the cylinder for illustrating the direct cylinder injection valve;
 Fig. 3 is a graph showing typical changes in the total conversion efficiency of NO_x and in the production rate of NH_3 of a three-way catalyst in accordance with the change in the excess air ratio of the exhaust gas;
 Fig. 4 is a graph showing a typical changes in the amount of NO_x produced in the cylinder and the amount of NH_3

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produced by a three-way catalyst in accordance with the changes in the excess air ratio of the combustion in the cylinder and the exhaust gas;

Fig. 5 is a graph showing the change in the amount of NH₃ produced by the three-way catalyst in accordance with the change in the excess air ratios of the combustion in the cylinder and the exhaust gas;

5 Fig. 6 is a flowchart explaining the exhaust gas purifying operation of the embodiment in Fig. 1;

Fig. 7 is a flowchart explaining the fuel injection control operation performed in the exhaust gas purifying operation in Fig. 6;

Fig. 8 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

10 Fig. 9 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 10 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 11 is a flowchart explaining the exhaust gas purifying operation of the embodiment in Fig. 10;

15 Fig. 12 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 13 is a flowchart explaining the exhaust gas purifying operation of the embodiment in Fig. 12;

Fig. 14 is a flowchart explaining the fuel injection control operation performed in the exhaust gas purifying operation in Fig. 12;

20 Fig. 15 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 16 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 17 is a flowchart explaining the exhaust gas purifying operation of the embodiment in Fig. 16;

25 Fig. 18 is a flowchart explaining the fuel injection control operation performed in the exhaust gas purifying operation in Fig. 16;

Fig. 19 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

30 Fig. 20 is a flowchart explaining the exhaust gas purifying operation of the embodiment in Fig. 19;

Figs. 21 and 22 are a flowchart explaining the fuel injection control operation performed in the exhaust gas purifying operation in Fig. 19;

35 Fig. 23 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 24 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 25 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

40 Fig. 26 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 27 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention;

Fig. 28 is a flowchart explaining the exhaust gas purifying operation of the embodiment in Fig. 23; and

45 Fig. 29 is a diagram explaining the changes in the amounts of NO_x absorbed in the NO_x absorbing-reducing catalysts during the exhaust gas purifying operation in Fig. 28.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Hereinafter, embodiments of the present invention will be explained, in detail, with reference to the accompanying drawings. In the accompanying drawings, the same reference numerals designate similar elements. In the embodiments explained hereinafter, Figs. 1, 8 through 10 and 23 through 26 show the embodiments in which all the exhaust gas from the cylinders flows through the NH₃ conversion means, and Figs. 12, 15, 16, 19 and 27 show the embodiments in which only the exhaust gas from specific cylinder(s) flows through the NH₃ conversion means and the exhaust gas which has passed through the NH₃ conversion means mixes with the exhaust gas from other cylinders.

Further, in the embodiments in Figs. 1, 8 through 10, 12, 15, 16 and 19, a three-way catalyst is used as NH₃ conversion means. In these embodiments, Figs. 1, 8, 12 and 15 represent the case where both of a NO_x absorbing-reducing catalyst and a NH₃ adsorbing-denitrating catalyst are used as the purification means. In contrast to this, only the NO_x absorbing-reducing catalyst is used in Fig. 10 and only the NH₃ adsorbing-denitrating catalyst is used in Figs. 10, 16 and 17 as the purification means.

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Further, in the embodiments in Figs. 23 through 27, the NO_x absorbing-reducing catalyst is used as the NH_3 conversion means. Namely, the NO_x absorbing-reducing catalysts in these embodiments are used as the NH_3 conversion means as well as the purification means.

5 The three-way catalyst, the NO_x absorbing-reducing catalyst and the NH_3 adsorbing-denitrating catalyst will be explained later in detail.

Hereinafter, the respective embodiments will be explained.

Fig. 1 shows the general configuration of an embodiment of the present invention when it is applied to a vehicle engine. In Fig. 1, reference numeral 1 designates a multi-cylinder type internal combustion engine for an automobile. In this embodiment, the engine 1 is a 4-cylinder engine having No. 1 through No. 4 cylinders. As explained later, each of 10 the cylinders is provided with a direct cylinder injection valve (71 through 74 in Fig. 1) which injects fuel directly into the cylinder and is operated at a lean air-fuel ratio during the normal operation of the engine. Namely, during the normal operation of the engine, the combustion in the cylinders of the engine is performed at a lean air-fuel ratio.

As can be seen from Fig. 1, the exhaust gas from No. 1 through No. 4 cylinders flows into a common exhaust gas passage 4 through an exhaust gas manifold 133. In the exhaust gas passage 4, a three-way catalyst 5 which acts as the NH_3 conversion means in this embodiment, and a NO_x absorbing-reducing catalyst 7 and a NH_3 adsorbing-denitrating catalyst 9, both act as purification means are disposed in this order from the upstream end.

15 Numeral 30 in Fig. 1 designates a control circuit of the engine 1. The control circuit 30 may, for example, consist of a microcomputer of a conventional type which comprises a ROM (read-only memory), a RAM (random access memory), a CPU (microprocessor). The control circuit 30 performs basic control of the engine such as a fuel injection control 20 and an ignition timing control.

25 Numeral 21 in Fig. 1 is an intake manifold connecting the intake port of the respective cylinders to a common intake air passage 2. The direct cylinder injection valve, as shown in Fig. 2, injects fuel directly into the cylinder in response to a fuel injection signal from the control circuit 30. In this embodiment, the direct cylinder injection valve of each cylinder injects fuel during the intake stroke or the compression stroke of the cylinder in order to cause the combustion of air-fuel mixture with a lean air-fuel ratio in the cylinder. This fuel injection performed during the intake stroke or the compression stroke in order to cause the combustion in the cylinder is hereinafter referred to as "the primary fuel injection".

30 Further, when it acts as the exhaust gas air-fuel ratio adjusting means, the direct cylinder injection valve injects fuel during the expansion stroke (preferably, during the latter half thereof) or the exhaust stroke of the cylinder in addition to the primary fuel injection. By performing fuel injection during the expansion stroke or the exhaust stroke, fuel is further 35 added to the combustion gas generated by the lean air-fuel ratio combustion in the cylinder and, thereby, the air-fuel ratio of the exhaust gas leaving the cylinder is adjusted to a rich air-fuel ratio. This fuel injection performed during the expansion stroke or the exhaust stroke in order to adjust the air-fuel ratio of the exhaust gas at a rich air-fuel ratio is hereinafter referred to as "the additional fuel injection". The fuel injected by the additional fuel injection does not burn in the cylinder, but is vaporized by the heat of the combustion gas in the cylinder and uniformly mixes with the combustion 40 gas in the cylinder. Therefore, a uniform mixture of exhaust gas and the vaporized fuel is discharged from the cylinder. Since the fuel injected by the additional fuel injection does not burn in the cylinder, it does not contribute to the generation of output torque at the cylinder. Therefore, the output torque of the respective cylinders stays the same even when the additional fuel injection is performed. Further, even when the additional fuel injection is performed only in the specific cylinder(s) of the engine, fluctuations in the engine output torque does not occur.

45 Usually, fuel such as gasoline or diesel fuel contains a large amount of hydrocarbons having relatively large molecular weights. When such fuel is injected into the cylinder by the additional fuel injection, a cracking of the heavy hydrocarbons occurs due to a high temperature and a high pressure in the cylinder, and hydrocarbons having smaller molecular weights are produced. These hydrocarbons having smaller molecular weights easily produce CO and H_2 in the exhaust gas by water gas reactions. Therefore, when the additional fuel injection is performed, the exhaust gas leaving the cylinders contains relatively large amounts of CO , H_2 and active light hydrocarbons.

50 In this embodiment, the primary fuel injection may be performed during the intake stroke of the cylinder in order to form a uniform air-fuel mixture with a lean air-fuel ratio in the cylinder. In this case, a lean air-fuel ratio combustion of a uniform air-fuel mixture occurs in the cylinder. Alternatively, the primary fuel injection may be performed during the period from the latter half of the intake stroke to the former half of the compression stroke in order to stratify a combustible air-fuel mixture near the ignition plug. In this case, a lean air-fuel ratio stratified charge combustion occurs in the cylinder.

Next, the three-way catalyst 5 in this embodiment will be explained.

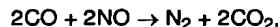
55 The three-way catalyst 5 uses, for example, a honeycomb type substrate made of cordierite, and a thin alumina layer, which acts as a carrier for the catalyst, is coated on the surface of the substrate. On this carrier, precious metals such as platinum Pt, rhodium Rh, and palladium Pd are attached. The three-way catalyst 5 converts HC , CO , NO_x in the exhaust gas with high efficiency when the air-fuel ratio of the exhaust gas is the stoichiometric air-fuel ratio (i.e., excess air ratio $\lambda = 1.0$). The conversion rates of HC and CO become higher than that of the stoichiometric air-fuel ratio when the air-fuel ratio becomes lean ($\lambda > 1.0$). Conversely, the conversion rate of NO_x becomes higher than that of the

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stoichiometric air-fuel ratio when the air-fuel ratio becomes rich ($\lambda < 1.0$).

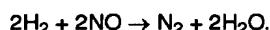
As stated before, most of the NO_x in the exhaust gas from the engine 1 consists of NO. When λ is smaller than 1.0 (i.e., when the air-fuel ratio of the exhaust gas is rich), a part of this NO is converted by the three-way catalyst 5 by reducing reactions

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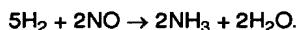


and

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However, a remaining part of NO is converted to NH_3 by the reaction



15

The conversion rate of NO to NH_3 becomes higher as the amount of rhodium Rh contained in the three-way catalyst increases. Further, as a catalytic component, palladium Pd shows a relatively high conversion rate of NO to NH_3 , and also shows a high oxidizing ability for HC and CO.

In this embodiment, since NH_3 is used for reducing NO_x on the denitrating catalyst 9 downstream of the three-way catalyst 5, it is preferable to produce as much NH_3 as possible at the three-way catalyst 5. Therefore, three-way catalyst 5 in this embodiment carries a relatively large amount of rhodium Rh or palladium Pd.

Fig. 3 shows the changes in the total conversion rate of NO_x (i.e., the ratio of the amount of NO_x converted to N_2 and NH_3 to the amount of NO_x flowing into the catalyst) and the production rate of NH_3 (i.e., the ratio of the amount of NO_x converted to NH_3 to the amount of NO_x flowing into the catalyst) of the three-way catalyst 5 in accordance with the change in the air-fuel ratio of the exhaust gas. As can be seen from Fig. 3, the total conversion rate of NO_x (the solid line in Fig. 3) rapidly decreases as the air-fuel ratio of the exhaust gas becomes larger than the stoichiometric air-fuel ratio ($\lambda = 1.0$). Therefore, when the exhaust gas flowing into the three-way catalyst 5 becomes lean ($\lambda > 1.0$), the amount of NO_x passing through the three-way catalyst 5 without being converted to N_2 and NH_3 rapidly increases.

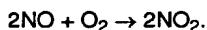
Conversely, when the air-fuel ratio becomes rich, the total conversion rate of NO_x increases and becomes almost 100% when the excess air ratio λ of the exhaust gas is smaller than approximately 0.95. Therefore, when the excess air ratio of the exhaust gas is smaller than 0.95, all of the NO_x in the exhaust gas flowing into the catalyst 5 is converted to N_2 and NH_3 , and the exhaust gas flowing out from the catalyst 5 does not contain NO_x .

The production rate of NH_3 (the broken line in Fig. 3) is almost zero when the air-fuel ratio becomes higher than the stoichiometric air-fuel ratio. However, in the region $\lambda < 1.0$, the production rate of NH_3 increases as the excess air ratio λ decreases, and becomes substantially constant in the region where $\lambda \leq 0.95$. Therefore, when the excess air ratio of the exhaust gas is in the region $\lambda \leq 0.95$, all of the NO_x is converted to N_2 and NH_3 and, further, the production rate of NH_3 becomes the maximum.

Next, the NO_x absorbing-reducing catalyst 7 in this embodiment will be explained.

The NO_x absorbing-reducing catalyst 7 in this embodiment uses, for example, an alumina as a carrier and, on this carrier, precious metals such as platinum Pt and at least one substance selected from alkali metals such as potassium K, sodium Na, lithium Li and cesium Cs; alkali-earth metals such as barium Ba and calcium Ca; and rare-earth metals such as lanthanum La and yttrium Y are carried. The NO_x absorbing-reducing catalyst 7 absorbs NO_x in the exhaust gas in the form of nitric acid ions when the air-fuel ratio of the exhaust gas is lean (i.e., when the excess air ratio λ is larger than 1.0), and releases the absorbed NO_x when the excess air ratio λ of the exhaust gas flowing the NO_x absorbing-reducing catalyst becomes smaller than 1.0 (i.e., the air-fuel ratio becomes rich).

Namely, considering the case where platinum Pt and barium Ba are carried on the NO_x absorbing-reducing catalyst 7, when the concentration of O_2 in the exhaust gas increases, i.e., when the excess air ratio λ of the exhaust gas becomes larger than 1.0, the oxygen O_2 in the exhaust gas is deposited on the surface of platinum Pt in the form of O_2^- or O_2^2- . The NO in the exhaust gas reacts with O_2^- or O_2^2- on the surface of the platinum Pt and becomes NO_2 by the reaction

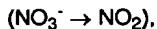


Then, NO_2 in the exhaust gas and the NO_2 produced on the platinum Pt are further oxidized on the surface of platinum Pt and absorbed into the catalyst while bonding with the barium oxide BaO and diffusing in the catalyst in the form of nitric acid ions NO_3^- . Thus, NO_x in the exhaust gas is absorbed by the NO_x absorbing-reducing catalyst 7 when the excess air ratio λ of the exhaust gas is larger than 1.0.

On the other hand, when the oxygen concentration in the exhaust gas becomes low, i.e., when the excess air ratio

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λ of the exhaust gas becomes $\lambda \leq 1.0$, the production of NO_2 on the surface of the platinum Pt is lowered and the reaction proceeds in an inverse direction



5 and thus nitric acid ions NO_3^- in the catalyst are released, in the form of NO_2 , from the NO_x absorbing-reducing catalyst 7.

7 In this case, if a reducing substance such as NH_3 , CO , H_2 , or a substance such as HC , CO_2 exist in the exhaust gas, released NO_x is reduced on the platinum Pt by these components.

10 As explained before, when the additional fuel injection is performed, the exhaust gas leaving the cylinders of the engine 1 contains a large amount of HC , CO , and CO_2 as well as H_2 produced by the water gas reactions. Further, in this condition, a part of NO_x in the exhaust gas reacts with H_2 and CO in the exhaust gas at the three-way catalyst 5 and produces NH_3 in the exhaust gas. Therefore, when the additional fuel injection is performed, the NO_x released from the NO_x absorbing-reducing catalyst 7 is reduced to N_2 by HC , CO , H_2 and NH_3 in the exhaust gas. Especially, since 15 the reducing ability of NH_3 is large, NO_x is reduced with high efficiency as the concentration of NH_3 in the exhaust gas becomes higher.

15 In addition, the NO_x absorbing-reducing catalyst also converts NO_x in the exhaust gas to NH_3 by a mechanism exactly the same as that of the three-way catalyst. Therefore, a NO_x absorbing-reducing catalyst can be used as the NH_3 conversion means in lieu of the three-way catalyst. Embodiments in which the NO_x absorbing-reducing catalyst is 20 used as the NH_3 conversion means will be explained later.

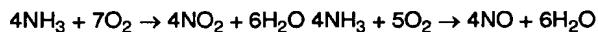
20 Next, the NH_3 adsorbing-denitrating catalyst 9 in this embodiment will be explained.

25 The NH_3 adsorbing-denitrating catalyst in the embodiments of the present invention uses, for example, a honeycomb type substrate made of cordierite, and an alumina layer which acts as a carrier for the catalyst is coated on the cell surface of the honeycomb substrate. On this carrier, at least one substance selected from elements belong to the fourth period or the eighth group in the periodic table of elements, such as copper Cu, chrome Cr, vanadium V, titanium Ti, iron Fe, nickel Ni, cobalt Co, platinum Pt, palladium Pd, rhodium Rh and iridium Ir are carried as a catalyst. Further, in this embodiment, "an NH_3 adsorbing substance", which is explained later, is also attached to the substrate of the NH_3 adsorbing-denitrating catalyst 9 in order to provide the catalyst 9 with an NH_3 adsorbing capability.

30 The NH_3 adsorbing-denitrating catalyst is capable of converting all the NH_3 in the exhaust gas flowing into the catalyst to N_2 provided the exhaust gas is in an oxidizing atmosphere (i.e., $\lambda > 1.0$) and the temperature of the catalyst is within a specific temperature range as determined by the substance being used as the catalyst. Namely, when the temperature of the NH_3 adsorbing-denitrating catalyst 9 is in the specific temperature range and the excess air ratio λ of the exhaust gas flowing into the catalyst is larger than 1.0, the denitrating reactions



occur in the NH_3 adsorbing-denitrating catalyst, in addition to the oxidizing reactions



45 Due to these denitrating reactions, the NO_x components produced by the oxidizing reactions are immediately converted to the N_2 component. As a result, of these sequential reactions, all of the NH_3 flowing into the NH_3 adsorbing-denitrating catalyst 9 is converted to N_2 .

50 Further, if the exhaust gas contains NO_x in addition to NH_3 , NO_x is reduced by the above-explained denitrating reactions to N_2 . In this case, if the amount of NH_3 in the exhaust gas is larger than the amount required to reduce all the NO_x contained in the exhaust gas, a surplus of NH_3 is converted to N_2 by the above-explained sequential oxidizing and denitrating reactions and does not pass through the NH_3 adsorbing-denitrating catalyst 9. Further, if HC and CO are contained in the exhaust gas in addition to NH_3 , HC and CO are oxidized by the NH_3 adsorbing-denitrating catalyst 9 and do not pass through the NH_3 adsorbing-denitrating catalyst provided the excess air ratio λ of the exhaust gas is larger than 1.0.

55 The specific temperature range explained above varies in accordance with the substance used as the catalyst. However, the specific temperature range of the NH_3 adsorbing-denitrating catalyst is generally lower than the temperature range where other catalysts such as the three-way catalyst are used. For example, the specific temperature range is approximately $100^\circ\text{C} - 400^\circ\text{C}$ when the substance such as platinum Pt, palladium Pd, rhodium Rh are used as the catalyst. More specifically, when platinum Pt is used, a temperature range $100^\circ\text{C} - 300^\circ\text{C}$ is more preferable, and a temperature range $150^\circ\text{C} - 250^\circ\text{C}$ is most preferable. When palladium Pd and rhodium Rh are used, a temperature range $150^\circ\text{C} - 400^\circ\text{C}$ is more preferable, and a temperature range $150^\circ\text{C} - 300^\circ\text{C}$ is most preferable. Further, when substances such as copper Cu, chrome Cr and iron Fe are used, the specific temperature range is approximately $150^\circ\text{C} -$

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650°C, and a temperature range 150°C - 500°C is preferable.

When the temperature of the NH₃ adsorbing-denitrating catalyst is above the specific temperature range, the oxidizing reactions become dominant in the catalyst and the amount of NH₃ which is oxidized by the catalyst increases. Thus, the denitrating reactions hardly occur in the catalyst due to the shortage of NH₃ in the exhaust gas, and the NO_x produced by the oxidizing reactions flows out from the NH₃ adsorbing-denitrating catalyst without being reduced by the denitrating reactions.

On the other hand, when the temperature of NH₃ adsorbing-denitrating catalyst is below the specific temperature range, the oxidizing reactions hardly occur due to the low temperature. This causes the NH₃ in the exhaust gas to pass through the NH₃ adsorbing-denitrating catalyst without being oxidized due to the shortage of NO_x produced by the oxidizing reactions.

In the embodiments explained below, the NH₃ adsorbing-denitrating catalyst 9 is disposed in the exhaust gas passage 4 at the position where the temperature of the catalyst 9 falls within the specific temperature range as explained above during the operation of the engine 1. The temperature of the NH₃ adsorbing-denitrating catalyst 9 may be controlled in the specific temperature range by providing a cooling water jacket or cooling fins to the NH₃ adsorbing-denitrating catalyst 9.

Next, the NH₃ adsorbing substance attached to the substrate of the catalyst 9 will be explained. It is known in the art that an acidic inorganic substance (which includes Broensted acids such as zeolite, silica SiO₂, silica-alumina SiO₂-Al₂O₃, and titania TiO₂ as well as Lewis acids including oxides of transition metals such as copper Cu, cobalt Co, nickel Ni and iron Fe) adsorb NH₃, and especially when the temperature is low, the substances adsorb a large amount of NH₃.

In this embodiment, one or more of these acidic inorganic substances is carried on the substrate of the NH₃ adsorbing-denitrating catalyst 9, or the substrate itself may be formed by a porous material made of such acidic inorganic substances. When the concentration of NH₃ in the exhaust gas is high, NH₃ in the exhaust gas is adsorbed by the acidic inorganic substance of the NH₃ adsorbing-denitrating catalyst 9, further, when the concentration of NH₃ in the exhaust gas becomes low, the NH₃ adsorbed in the acidic inorganic substance is released. Therefore, the NH₃ adsorbing-denitrating catalyst 9 is capable of reducing NO_x by the denitrating reactions, even when NH₃ does not exist in the exhaust gas, using the NH₃ it has adsorbed when the NH₃ concentration was high.

As an NH₃ adsorbing-denitrating catalyst 9, other types of catalyst may be used. For example, a catalyst which uses, for example, zeolite ZSM-5 as a substrate, with metals such as copper Cu, iron Fe or platinum Pt attached thereto by an ion exchange method (a copper-zeolite catalyst, an iron-zeolite catalyst, platinum-zeolite catalyst, respectively) may be used as the NH₃ adsorbing-denitrating catalyst. Alternatively, a substrate made of zeolite such as mordenite and a precious metal such as platinum Pt and/or other metals attached thereon (for example, a platinum-mordenite catalyst or a platinum-copper-mordenite catalyst) can also be used as the NH₃ adsorbing-denitrating catalyst. These zeolite NH₃ adsorbing-denitrating catalysts trap NH₃, HC and CO components in the exhaust gas in the pores of the porous zeolite, and selectively reduce NO_x in the exhaust gas using these trapped components (as well as NH₃, HC, CO in the exhaust gas) even in an oxidizing atmosphere.

Next, the exhaust gas purifying operation of the embodiment in Fig. 1 will be explained.

In the explanation hereinafter, the term "an air-fuel ratio of the combustion" (or "an excess air ratio of the combustion") means an air-fuel ratio (an excess air ratio) of the air-fuel mixture in the whole cylinder in the case where the combustion of the uniform air-fuel mixture as explained before takes place in the cylinder and, an air-fuel ratio (an excess air ratio) of the stratified air-fuel mixture in the case where the stratified charge combustion takes place in the cylinder.

In the embodiment in Fig. 1, all of the No. 1 through No. 4 cylinders are operated at a lean air-fuel ratio during the normal operation. In this case, the excess air ratio of the combustion in the respective cylinders is set at a value at which the amount of NO_x produced by the combustion becomes as small as possible (for example, $\lambda \approx 1.4$). Further, the additional fuel injection is not performed during the normal operation. Therefore, the exhaust gas leaving the cylinders during the normal operation is at a lean air-fuel ratio and contains a relatively small amount of NO_x. This lean air-fuel ratio exhaust gas flows into the three-way catalyst 5 during the normal operation. However, since the conversion efficiency of NO_x falls rapidly when the air-fuel ratio of the exhaust gas is lean as explained in Fig. 3, a large part of the NO_x in the exhaust gas passes through the three-way catalyst 5 without being reduced and flows into the NO_x absorbing-reducing catalyst 7. Since the NO_x absorbing-reducing catalyst 7 absorbs NO_x when the exhaust gas is at a lean air-fuel ratio, the NO_x passing through the three-way catalyst 5 without being reduced is absorbed in the NO_x absorbing-reducing catalyst 7.

Namely, NO_x produced by the lean air-fuel ratio combustion in the cylinder during the normal operation is stored temporarily in the NO_x absorbing-reducing catalyst 7. Therefore, if the normal operation of the engine continues for a long time, the amount of the NO_x absorbed in the NO_x absorbing-reducing catalyst 7 increases and this may cause the NO_x absorbing-reducing catalyst to be saturated with the absorbed NO_x. In order to prevent this problem, the additional fuel injection is performed on all cylinders for a short period when the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst 7 increases. By performing the additional fuel injection, the air-fuel ratio of the exhaust gas from the cylinders shifts to a rich air-fuel ratio, and a part of NO_x in the exhaust gas is converted into NH₃ on the three-way cat-

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alyst 5. Thus, when the additional fuel injection is started, a rich air-fuel ratio exhaust gas containing a relatively large amount of NH_3 flows into the NO_x absorbing-reducing catalyst 7 and, thereby, the NO_x absorbed in the NO_x absorbing-reducing catalyst 7 is released due to the rich air-fuel ratio exhaust gas and is reduced by NH_3 , HC and CO in the exhaust gas.

5 As explained above, NO_x absorbed in the NO_x absorbing-reducing catalyst 7 is released and reduced by shifting the air-fuel ratio of the exhaust gas to a rich air-fuel ratio by performing the additional fuel injection periodically for a short time during the normal operation. In this specification, the operation for shifting the air-fuel ratio of the exhaust gas to a rich air-fuel ratio in order to cause the NO_x absorbing-reducing catalyst 7 to release the absorbed NO_x is referred to as "a rich spike operation".

10 In order to reduce all of the NO_x released from the NO_x absorbing-reducing catalyst 7, a large amount of NH_3 is required during the rich spike operation. Therefore, the air-fuel ratio of the combustion in the cylinder during the rich spike operation is set at a value where the amount of NO_x produced by the combustion becomes the maximum (for example, at the excess air ratio $\lambda = 1.4$) in order to increase the amount of NO_x supplied to three-way catalyst 5 and converted into NH_3 thereon. Further, the amount of additional fuel injection is set in such a manner that the air-fuel ratio 15 of the exhaust gas after the additional fuel injection becomes a value where the conversion rate of NO_x into NH_3 by the three-way catalyst 5 becomes the maximum (for example, at the excess air ratio $\lambda = 0.95$).

20 Next, the function of the NH_3 adsorbing-denitrating catalyst 9 in this embodiment will be explained. In this embodiment, a relatively large amount of NH_3 is produced at the three-way catalyst 5 during the rich spike operation. Therefore, in some cases, a surplus of NH_3 , which is not used for reducing NO_x on the NO_x absorbing-reducing catalyst 7 passes through the NO_x absorbing-reducing catalyst 7. This surplus of NH_3 is adsorbed by the NH_3 adsorbing-denitrating catalyst 9 and stored temporarily therein. On the other hand a small amount of NO_x also passes through the NO_x absorbing-reducing catalyst 7 during the normal operation and flows into the NH_3 adsorbing-denitrating catalyst 9. In this embodiment, NO_x passing through the NO_x absorbing-reducing catalyst 7 during the normal operation is reduced by the NH_3 adsorbing-denitrating catalyst 9 using the NH_3 adsorbed and stored therein during the rich spike operation. 25 Therefore, in this embodiment, the total conversion efficiency of NO_x is improved by the NH_3 adsorbing-denitrating catalyst 9 disposed in the exhaust gas passage downstream of the NO_x absorbing-reducing catalyst 7.

25 As explained above, the amount of NH_3 produced by the three-way catalyst 5 largely increases by performing the additional fuel injection. The reason why the amount of the NH_3 production increases due to the additional fuel injection will be explained with reference to Figs. 4 and 5.

30 In Fig. 4, the broken line represents the change in the amount (the concentration) of NO_x produced by the combustion in the cylinder in accordance with the change in the excess air ratio λ of the combustion. As can be seen from Fig. 4, the amount of the NO_x production increases as the excess air ratio λ becomes large in the region where the λ is relatively small. The amount of the NO_x production in the exhaust gas reaches its maximum value at $\lambda = 1.2$ and, in the region where $\lambda \geq 1.2$, the NO_x production decreases as the λ increases. In the embodiment in Fig. 1, since the excess air ratio of the exhaust gas flowing into the three-way catalyst 5 is the same as the excess air ratio of the combustion in the cylinder when the additional fuel injection is not performed, the amount of NO_x in the exhaust gas flowing into the three-way catalyst 5 changes in accordance with the excess air ratio λ as shown by the broken line in Fig. 4 when the additional fuel injection is not performed. As explained before, the production rate of NH_3 by the three-way catalyst 5 (i.e., the ratio of the amount of NO_x converted to NH_3 to the amount of NO_x flowing into the catalyst 5) changes in 35 accordance with the excess air ratio of the exhaust gas as shown in Fig. 3. Since the amount of NH_3 actually produced at the three-way catalyst 5 is given by the product of the amount of NO_x in the exhaust gas (the broken line in Fig. 4) and the production rate of NH_3 (the broken line in Fig. 3), the amount of NH_3 actually produced at the three-way catalyst changes in accordance with the excess air ratio λ of the combustion as shown by the solid line in Fig. 4. Namely, as can be seen from the solid line in Fig. 4, when the excess air ratio λ of the combustion is larger than 1.0, NH_3 is not produced 40 at all even though the amount of NO_x produced by the combustion is relatively large. In contrast to this, when the λ of the combustion is smaller than 1.0, though the production rate of NH_3 of the three-way catalyst increases, the amount of NO_x actually produced by the three-way catalyst 5 becomes relatively small since the amount of NO_x produced by the combustion becomes small in this region of λ . Further, though the production rate of NH_3 becomes maximum when the excess air ratio λ becomes smaller than about 0.95, since the amount of NO_x in the exhaust gas further decreases, 45 the amount of the NH_3 production decreases as the excess air ratio λ of the combustion decreases. Therefore, as can be seen from the solid line in Fig. 4, though the amount of NH_3 produced by the three-way catalyst becomes the maximum at $\lambda = 0.95$, the amount of NH_3 actually produced is small even at $\lambda = 0.95$.

50 Thus, when the excess air ratio of the combustion in the cylinder and the excess air ratio of the exhaust gas flowing into the three-way catalyst 5 is the same, the excess air ratio of the combustion must be set at the value smaller than 1.0 in order to produce NH_3 at the three-way catalyst 5. This causes the decrease in the amount of NO_x produced in the cylinder, and the amount of NH_3 actually produced at the three-way catalyst 5 also decreases due to the decrease in the raw material (NO_x) in the exhaust gas used for producing NH_3 .

55 Fig. 5 is a graph similar to Fig. 4, showing the amount of NH_3 produced by the three-way catalyst 5 when the addi-

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tional fuel injection is performed. By performing the additional fuel injection, the excess air ratio of the exhaust gas flowing into the three-way catalyst 5 can be changed independently from the excess air ratio of the combustion in the cylinder. Therefore, the excess air ratio of the exhaust gas flowing into the three-way catalyst 5 can be set at 0.95 where the production rate of NH_3 becomes the maximum while fixing the excess air ratio of the combustion in the cylinder at 1.2 where the amount of NO_x produced by the combustion becomes the maximum. The solid line in Fig. 5 represents the amount of NH_3 produced at the three-way catalyst 5 when the excess air ratio of the combustion in the cylinder is fixed at $\lambda = 1.2$. In this case, the amount of NH_3 produced at the catalyst 5 changes in the manner similar to the solid line in Fig. 3 and, when the excess air ratio of the exhaust gas flowing into the catalyst 5 becomes lower than about 0.95, a large amount of NH_3 is produced by the three-way catalyst 5.

Further, when the additional fuel injection is performed, the amount of the smaller molecular weight hydrocarbons increases due to the cracking of fuel injected by the additional fuel injection. Smaller molecular weight (light) hydrocarbons have higher activities compared to heavy hydrocarbons and readily produce CO and H_2 , by the water gas reactions, on the three-way catalyst. As explained before, CO and H_2 are required for converting NO_x to NH_3 . Therefore, since the amount of CO and H_2 are also increased due to the additional fuel injection, the amount of NH_3 produced at the three-way catalyst further increases due to the additional fuel injection. Further, the light hydrocarbons, CO and H_2 in the exhaust gas are very capable of reducing NO_x by themselves on the NO_x absorbing-reducing catalyst and NH_3 adsorbing-denitrating catalyst. Therefore, light hydrocarbons, CO and H_2 produced by the additional fuel injection are utilized to reduce NO_x at the NO_x absorbing-reducing catalyst and NH_3 adsorbing-denitrating catalyst even if those components are not converted into NH_3 at the three-way catalyst.

In the embodiment in Fig. 1, the excess air ratio of the combustion in the cylinders is set at $\lambda = 1.2$ during the rich spike operation, and the excess air ratio of the exhaust gas flowing into the three-way catalyst 5 is adjusted at $\lambda = 0.95$ by the additional fuel injection in order to increase the amount of NH_3 produced at the three-way catalyst 5 to the maximum.

Fig. 6 is a flowchart explaining the exhaust gas purifying operation of the present embodiment. This operation is performed by a routine executed by the control circuit 30 at predetermined intervals.

In Fig. 6, at step 601, the operation determines whether the value of a lean operation flag FL is set at 1. The value of the lean operation flag FL represents whether the rich spike operation (and the additional fuel injection) should be performed and, $\text{FL} = 1$ means that the rich spike operation should not be performed. When $\text{FL} = 1$ at step 601, this means that the exhaust gas with the excess air ratio same as that of the combustion in the cylinders flows into the three-way catalyst 5. The value of the flag FL is set at steps 609 and 617 as explained later.

If $\text{FL} = 1$ at step 601, the operation performs step 603 and 605 to calculate the amount FNOX of NO_x absorbed and stored in the NO_x absorbing-reducing catalyst 7.

In this embodiment, the amount of NO_x produced by the engine 1 per unit time (ANOX) is actually measured beforehand by operating the actual engine under various engine load conditions (such as air intake amount Q , engine speed N), and the measured amounts of produced NO_x are stored in the ROM of the ECU 30 in the form of a numerical table using the engine air intake amount Q and speed N as parameters. At step 603, the amount of NO_x (ANOX) produced by the engine per unit time is determined from this numerical table based on Q and N . The unit time used for measuring ANOX is set at, for example, a time the same as the interval of the execution of the routine for performing the operation in Fig. 6. At step 605, the amount FNOX of NO_x stored in the NO_x absorbing-reducing catalyst is obtained by accumulating the values of ANOX. The amount of NO_x absorbed in the NO_x absorbing-reducing catalyst per unit time is proportional to the amount of NO_x flows into the catalyst per unit time (i.e. ANOX). Since FNOX is the integrated value of ANOX, the value of FNOX represents the amount of NO_x stored in the NO_x absorbing-reducing catalyst.

After calculating the amount FNOX , the operation determines whether the amount FNOX , i.e., the amount of NO_x stored in the NO_x absorbing-reducing catalyst 7 reaches a predetermined value FNOX_0 . The value FNOX_0 corresponds to an amount of the absorbed NO_x where the capability of the NO_x absorbing-reducing catalyst for absorbing NO_x in the exhaust gas starts to decrease and, in this embodiment, is set at a value around 70% of the maximum amount of NO_x which the NO_x absorbing-reducing catalyst can store (i.e., about 70% of the saturating amount). If $\text{FNOX} < \text{FNOX}_0$ at step 607, since the NO_x absorbing-reducing catalyst still has a sufficient capacity for absorbing NO_x in the exhaust gas, the operation immediately terminates, i.e., the lean air-fuel ratio operation of the engine is continued.

However, if $\text{FNOX} \geq \text{FNOX}_0$ at step 607, since the ability of the NO_x absorbing-reducing catalyst started to decrease due to the increase in the absorbed NO_x , the operation performs step 609 to reset the value of the lean operation flag FL to 0 and step 611 to determine the value of a counter CT which represents the length of the period for performing the rich spike operation.

The value of the counter CT , i.e., the length of the period for performing the rich spike operation must be determined in such a manner that the total amount of NH_3 , HC and CO produced by the additional fuel injection during the rich spike operation is sufficiently large for reducing the amount of NO_x stored in the NO_x absorbing-reducing catalyst 7. Though the amount of the NO_x when the rich spike operation starts is a fixed value (for example, about 70% of the saturation amount), the amount of NO_x and HC , CO produced by the engine per unit time varies depending on the operating con-

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dition (air intake amount Q and engine speed N) of the engine during the rich spike operation. Therefore, the amount of NH_3 produced at the three-way catalyst 5 per unit time also varies depending on the operating condition of the engine. Thus, in this embodiment, the length of the period for performing the rich spike operation is changed in accordance with the operating condition of the engine so that a sufficient amount of NH_3 , for reducing all the NO_x stored in the NO_x absorbing-reducing catalyst 7 is produced during the rich spike operation. For example, when the amount of NO_x produced by the engine per unit time is small, the length of the period for performing the rich spike operation (the additional fuel injection) must be set longer, and if the amount of NO_x produced by the engine per unit time is large, the length of the period must be set shorter in this embodiment.

In this embodiment, the amount of NH_3 required for reducing the amount of NO_x corresponding to the value FNOX_0 of the counter FNOX is measured previously, and the time required for producing this amount of NH_3 on the NH_3 conversion means are measured by operating the engine under various load conditions. The measured time required for producing the required amount of NH_3 for reducing the amount of NO_x corresponding to the value FNOX_0 is stored in the ROM of the control circuit 30 in the form of a numerical table using Q and N as parameters. The required time CT is determined from Q and N at step 611 using this numerical table.

When the value of the lean operation flag FL is set to 0 (step 609), step 613 is performed after step 601 when the operation is next performed. In the steps 613 through 619, the value of the counter CT is reduced by Δt every time the operation is performed at step 615 (Δt is the interval of the execution of the operation). When the time CT has elapsed, i.e., when the value of the CT becomes less than 0 at step 613, the value of the lean operation flag FL is set to 1 at step 617. Further, the counter FNOX which represents the amount of NO_x stored in the NO_x absorbing-reducing catalyst 7 is reset to 0 at step 619. By the operation in Fig. 6, the rich spike operation is performed for a time period CT determined by the engine operating condition. During the rich spike operation, the additional fuel injection is performed for adjusting the air-fuel ratio of the exhaust gas to a rich air-fuel ratio. Therefore, the exhaust gas with a rich air-fuel ratio and containing a large amount of NO_x flows into the three-way catalyst 5 and, thereby, a large amount of NH_3 is produced at the three-way catalyst 5. Thus, the exhaust gas flowing through the three-way catalyst 5 which contains a large amount of NH_3 is supplied to the NO_x absorbing-reducing catalyst 7, and the NO_x released from the NO_x absorbing-reducing catalyst 7 is reduced by reacting with NH_3 in the exhaust gas.

When the predetermined time CT has elapsed, the lean operation flag FL is set to 1 (step 617), and the lean air-fuel ratio operation of the engine is resumed. Thus, the NO_x absorbing-reducing catalyst 7, after releasing and reducing all the absorbed NO_x , restarts the absorbing of NO_x in the exhaust gas.

Fig. 7 is a flowchart explaining the fuel injection control operation in the present embodiment. This operation is performed by a routine executed by the control circuit 30 at a predetermined rotation angle of the crankshaft of the engine 1.

In Fig. 7, at step 701, the operation determines whether the value of the lean operation flag FL is set at 1. The fuel injection is performed in steps 703 through 715 in accordance with the value of the flag FL .

When $FL = 1$ at step 701, i.e., when the rich spike operation is not performed, the excess air ratio λ_B of the combustion of the respective cylinders is set at λ_{LL} at step 703. λ_{LL} is an excess air ratio of the combustion where the amount of NO_x produced by the combustion becomes small and, in this embodiment, λ_{LL} is set at about 1.4. If $FL \neq 1$ at step 701, i.e., if the rich spike operation is being performed, λ_B of the respective cylinders is set at a value λ_L where the amount of NO_x produced by the combustion becomes the maximum ($\lambda_L = 1.2$).

When the excess air ratio λ_B of the respective cylinders is set at either of steps 703 and 705, the fuel injection amount required for setting the excess air ratio of the combustion at λ_B is calculated by the fuel injection amount calculating operation (not shown) performed by the control circuit 30. In this embodiment, the required fuel injection amount is calculated based on, for example, an air intake amount per one revolution of the engine (Q/N).

Then, at step 707, the operation determines whether it is the primary fuel injection timing of any one of the cylinders. If it is the primary fuel injection timing of any of the cylinders, the primary fuel injection is performed in that cylinder. Thus, combustion with the excess air ratio λ_B is performed in the cylinder. If it is not the primary fuel injection timing of any of the cylinders, the operation executes step 711 to determine whether an additional fuel injection is required, based on the value of the flag FL . If $FL \neq 1$ at step 711, since this means that the additional fuel injection is required, the operation proceeds to step 713 to determine whether it is the timing for the additional fuel injection of any of the cylinders. If it is the additional fuel injection timing of any of the cylinders, the additional fuel injection is performed in that cylinder at step 715. The amount of additional fuel injection is determined by the operation performed by the control circuit 30 (not shown) so that the excess air ratio of the exhaust gas leaving the cylinder becomes the value λ_A where the production rate of NH_3 by the three-way catalyst 5 becomes the maximum (for example, $\lambda_A = 0.95$).

As explained above, in the operations in Figs. 6 and 7, the additional fuel injection is performed in the respective cylinders every time the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst 7 reaches a predetermined value, in order to release NO_x from the NO_x absorbing-reducing catalyst and reduce the same. The length of the period for performing the additional fuel injection is determined in accordance with the operating condition of the engine such as the amount of NO_x produced by the engine per unit time.

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Further, though the total amount of NH₃ produced by the three-way catalyst 5, i.e., the total amount of NH₃ supplied to the NO_x absorbing-reducing catalyst 7, is controlled by adjusting the length of the period for performing additional fuel injection, the total amount of NH₃ supplied to the NO_x absorbing-reducing catalyst may be controlled by adjusting the air-fuel ratio of the exhaust gas flowing into the three-way catalyst 5. Namely, as can be seen from Fig. 5, the production rate of NH₃ of the three-way catalyst 5 can be changed between 0 and its maximum value by changing the excess air ratio of the exhaust gas within the range $\lambda = 0.95 - 1.0$. Therefore, the total amount of NH₃ produced by the three-way catalyst may be controlled by adjusting the excess air ratio of the exhaust gas flowing into the three-way catalyst within the range $\lambda = 0.95 - 1.0$. Since the amount of NH₃ produced by the three-way catalyst 5 per unit time changes in accordance with the excess air ratio of the exhaust gas, the total amount of NH₃ produced by the three-way catalyst 5 can be adjusted by changing the excess air ratio of the exhaust gas without changing the length of the period for performing the additional fuel injection. In this case, for example, the value of CT is set at a constant at step 611 in Fig. 6. Further, the operation calculates the required production rate of NH₃ based on the amount of NH₃ required for reducing the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst and the fixed time CT. The additional fuel injection amount is determined in such a manner that the excess air ratio λ_A of the exhaust gas flowing into the three-way catalyst 5 becomes a value which gives the required production rate of NH₃.

In this embodiment, the three-way catalyst 5, NO_x absorbing-reducing catalyst 7 and NH₃ adsorbing-denitrating catalyst 9 are disposed in the exhaust gas passage 4 in this order from the upstream end. In this arrangement, the NO_x absorbing-reducing catalyst 7 mainly purifies NO_x in the exhaust gas, and the NH₃ adsorbing-denitrating catalyst 9 only purifies a small amount of NO_x passing through the NO_x absorbing-reducing catalyst 7. However, the positions of the NO_x absorbing-reducing catalyst 7 and the NH₃ adsorbing-denitrating catalyst 9 may be interchanged. Namely, the three-way catalyst 5, the NH₃ adsorbing-denitrating catalyst 9 and NO_x absorbing-reducing catalyst 7 may be disposed in the exhaust gas passage 4 in this order from the upstream end, as shown in Fig. 8. In this case, the NH₃ adsorbing-denitrating catalyst 9 mainly purifies NO_x in the exhaust gas. During the normal operation (i.e., when the rich spike operation is not performed), since the air-fuel ratio of the exhaust gas flowing into the three-way catalyst 5 is lean, NH₃ is not produced at the three-way catalyst 5. Therefore, the NH₃ adsorbing-denitrating catalyst 9 purifies NO_x in the exhaust gas during the normal operation using NH₃ it has adsorbed and stored therein. Thus, the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 decreases during the normal operation of the engine. Further, the NO_x absorbing-reducing catalyst 7 absorbs NO_x passing through the NH₃ adsorbing-denitrating catalyst 9 without being reduced during the normal operation. Thus, the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst 7 gradually increases during the normal operation. Therefore, in this case, the rich spike operation is performed when the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 decreases to a predetermined value. When the rich spike operation is performed, NH₃ is produced at the three-way catalyst and the exhaust gas with a rich air-fuel ratio and containing NH₃ flows into the NH₃ adsorbing-denitrating catalyst 9. This causes the NH₃ adsorbing-denitrating catalyst 9 to adsorb NH₃ in the exhaust gas. Further, a rich air-fuel ratio exhaust gas containing a surplus of NH₃ flows into the downstream NO_x absorbing-reducing catalyst 7, NO_x absorbed in the NO_x absorbing-reducing catalyst is released and reduced by the rich air-fuel ratio exhaust gas containing NH₃. The detail of the exhaust gas purifying operation of the embodiment in Fig. 8 will be explained later using Fig. 11.

Fig. 9 is a drawing similar to Fig. 1 showing the general configuration of another embodiment of the present invention. The arrangement of Fig. 9 is different from that of Fig. 1 in that the NH₃ adsorbing-denitrating catalyst 9 in Fig. 1 is removed in Fig. 9. Namely, only the three-way catalyst 5 and the NO_x absorbing-reducing catalyst 7 are disposed in the exhaust gas passage 4 from the upstream end in this order in Fig. 9. Since the NH₃ adsorbing-denitrating catalyst 9 in the embodiment in Fig. 1 only acts as an ancillary means for purifying NO_x in the exhaust gas, the efficiency for purifying NO_x does not lower largely even if the NH₃ adsorbing-denitrating catalyst 9 is removed. Therefore, by using only the three-way catalyst 5 and the NO_x absorbing-reducing catalyst 7 as shown in Fig. 9, the exhaust gas purification device can be largely simplified. The exhaust gas purifying operation of the embodiment in Fig. 9 is the same as those in Figs. 6 and 7.

Next, another embodiment of the present invention is explained with reference to Fig. 10. As can be seen from Fig. 10, the NO_x absorbing-reducing catalyst 7 is not provided in this embodiment, and only the three-way catalyst 5 and the NH₃ adsorbing-denitrating catalyst 9 are disposed in the exhaust gas passage 4 in this order from the upstream end.

As explained before, the NH₃ adsorbing-denitrating catalyst 9 is capable of reducing NO_x in the exhaust gas by reacting NO_x with NH₃. Further, since the NH₃ adsorbing-denitrating catalyst is capable of adsorbing and storing NH₃ in the exhaust gas which is not used for reducing NO_x, the NH₃ adsorbing-denitrating catalyst is also capable of reducing NO_x using NH₃ adsorbed and stored therein even when NH₃ is not contained in the exhaust gas. In this embodiment, the rich spike operation is performed for producing NH₃ at the three-way catalyst 5 and for causing the NH₃ adsorbing-denitrating catalyst 9 to adsorb and store NH₃. The NH₃ adsorbing-denitrating catalyst 9 reduces NO_x in the lean air-fuel ratio exhaust gas during the normal operation using NH₃ stored therein. Therefore, NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 is used for reducing NO_x in the exhaust gas and decreases during the normal operation. Therefore, it is necessary to replenish NH₃ adsorbing-denitrating catalyst 9, with NH₃, before it uses up all the

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stored NH₃.

In the exhaust gas purifying operation of the present embodiment, the operation estimates the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 during the normal operation of the engine. When the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst decreases to a predetermined value, the operation performs rich spike operation in order to replenish the NH₃ adsorbing-denitrating catalyst with NH₃. Thus, according to this embodiment, a shortage of NH₃ required for reducing NO_x in the exhaust gas does not occur.

5 Fig. 11 is a flowchart explaining the exhaust gas purifying operation of the present embodiment. This operation is performed by a routine executed by the control circuit 30 at predetermined intervals.

In the operation in Fig. 11, the operation estimates the amount of NH₃ (INH₃) stored in the NH₃ adsorbing-denitrating catalyst 9 based on the amount of NO_x produced by the engine per unit time (ANOX). Further, when INH₃ decreases to a lower limit I₀, the operation performs the rich spike operation in order to increase the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst to the value IFUL near the saturation amount.

10 In Fig. 11, at step 1101, the operation determines whether the lean operation flag FL is set to 1. If FL = 1, then, the operation continues the lean air-fuel ratio operation of the engine and calculates ANOX (the amount of NO_x produced by the engine per unit time) based on the air intake amount Q and the engine speed N at step 1103. Steps 1101 and 1103 are operations the same as steps 601 and 603 in Fig. 6. At step 1105, INH₃ (the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9) is calculated by $INH_3 = INH_3 - K \times ANOX$. During the lean air-fuel ratio operation, the NH₃ adsorbing-denitrating catalyst 9 reduces NO_x in the exhaust gas using NH₃ stored in the catalyst 9. Therefore, the decrease in the NH₃ held in the NH₃ adsorbing-denitrating catalyst 9 per unit time is proportional to the amount of NO_x produced by the engine per unit time. Thus, if the amount ANOX of NO_x is produced by the engine per unit time, the amount of NO_x held (stored) in the NH₃ adsorbing-denitrating catalyst 9 decreases by $K \times ANOX$ per unit time (K is a constant). Therefore, the amount of NO_x held in the NH₃ adsorbing-denitrating catalyst 9 is obtained by subtracting ($K \times ANOX$) from the value INH₃ at step 1105.

15 At step 1107, the operation determines whether the amount INH₃ calculated at step 1105 decreases to a predetermined value I₀. The value I₀ is, for example, set at 20 to 30% of the maximum amount of NH₃ which the NH₃ adsorbing-denitrating catalyst can hold (i.e., 20 to 30% of the saturating amount). If $INH_3 > I_0$ at step 1107, the operation continues the lean air-fuel ratio operation of the engine 1. However, if $INH_3 \leq I_0$ at step 1107, the operation performs the rich spike operation of the engine to supply NH₃ to the NH₃ adsorbing-denitrating catalyst 9.

20 In this case, the lean operation flag FL is set to 0 at step 1109, and the length CTH of the period for performing the additional fuel injection is determined at step 1111 in accordance with the air intake amount Q and speed N of the engine 1. As explained in Fig. 6, the amount of NH₃ produced by the three-way catalyst 5 per unit time during the rich spike operation changes in accordance with the engine operating condition (i.e., the amount of NO_x produced by the engine per unit time). Further, in this embodiment, it is necessary to supply the amount of NO_x sufficient for increasing the NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 from the lower limit I₀ to the maximum value IFUL during the rich spike operation. Therefore, the length CTH of the period for performing the additional fuel injection is determined based on the amount of NO_x produced by the engine per unit time. The period CTH is the time sufficient for increasing the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 from I₀ to IFUL. The value of CTH is measured previously by operating the actual engine under various conditions of the air intake amount Q and the speed N, and stored in the ROM of the control circuit 30 in the form of a numerical table using Q and N as parameters. At step 1111, 25 CTH is determined from the air intake amount Q and the speed N based on the numerical table.

30 When the lean operation flag FL is set to 0 at step 1109, step 1113 is executed after step 1101 when the operation is next performed, and the additional fuel injection is performed for the period CTH. When the time CTH has elapsed (step 1113), the lean operation flag FL is set to 1 (step 1117) to terminate the additional fuel injection, and the value of the counter INH₃ which represents the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 is set to IFUL (step 1119). The fuel injection control operation in Fig. 7 is performed also in this embodiment in order to perform the primary fuel injection and/or the additional fuel injection according to the value of the lean operation flag FL.

35 As explained above, in the operations in Fig. 11 and Fig. 7, the additional fuel injection of the respective cylinders is performed when the amount of NH₃ stored in the NH₃ adsorbing-denitrating catalyst 9 decreases to a predetermined value, and increases the amount of NH₃ in the NH₃ adsorbing-denitrating catalyst 9 to a value near the saturating amount. Further, the period for performing the additional fuel injection is determined in accordance with the engine operating condition such as the amount of NO_x produced by the engine per unit time.

40 Further, as explained before, the operations of Figs. 11 and 7 are performed also in the embodiment in Fig. 8. The amount of the additional fuel injection instead of the length CTH of the period for performing the additional fuel injection may also be adjusted in accordance with the engine operating condition in the embodiment in Fig. 10.

45 Next, embodiments different from the embodiments in Figs. 1 and 8 through 10 will be explained using Figs. 12 through 22. In the embodiments in Figs. 1 and 8 through 10, the exhaust gas from all of the cylinders flows through the three-way catalyst 5 which acts as the NH₃ conversion means. However, in the embodiments explained hereinafter, the exhaust gas from only some of the cylinders flows through the NH₃ conversion means.

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First, the embodiment in Fig. 12 will be explained.

As can be seen from Fig. 12, No. 1 cylinder of the engine 1 is directly connected to a three-way catalyst 5 via an exhaust gas passage 143, and No. 2 through No. 4 cylinders are connected to a NO_x absorbing-reducing catalyst 7 via an exhaust manifold 131. The three-way catalyst 5 and the NO_x absorbing-reducing catalyst 7 are connected to a common exhaust gas passage 4 through exhaust gas passages 142 and 141 downstream thereof, respectively. An NH_3 adsorbing-denitrating catalyst 9 is disposed in the common exhaust gas passage 4. Namely, NH_3 produced by the three-way catalyst 5 is supplied only to the NH_3 adsorbing-denitrating catalyst 9 in this embodiment. Further, the additional fuel injection is performed on No. 1 cylinder during the normal operation as well as during the rich spike operation of the engine in this embodiment.

The exhaust gas purifying operation in this embodiment is now explained.

In the normal operation, No. 2 through No. 4 cylinders are operated at an excess air ratio where the amount of NO_x produced by the combustion becomes the minimum (for example, excess air ratio about 1.4). Therefore, the air-fuel ratio of the exhaust gas flowing into the NO_x absorbing-reducing catalyst 7 from No. 2 through No. 4 cylinders are lean during the normal operation. Thus, NO_x produced in No. 2 through No. 4 cylinders during the normal operation is absorbed by the NO_x absorbing-reducing catalyst 7 and removed from the exhaust gas.

On the other hand, No. 1 cylinder is always operated at an excess air ratio where the amount of NO_x produced by the combustion becomes the maximum (for example, excess air ratio about 1.2) in this embodiment. Further, the additional fuel injection is always performed on the No. 1 cylinder to adjust the excess air ratio of the exhaust gas from No. 1 cylinder at a value where the production rate of NH_3 by the three-way catalyst 5 becomes the maximum (for example, the excess air ratio about 0.95). Thus, a part of NO_x in the exhaust gas from No. 1 cylinder is reduced at the three-way catalyst 5, and a portion of the remaining part of NO_x is converted into NH_3 . Namely, a relatively large amount of NH_3 is produced at the three-way catalyst 5.

The exhaust gas from the NO_x absorbing-reducing catalyst 7 and the exhaust gas from the three-way catalyst 5 flow into the common exhaust gas passage 4 through the exhaust gas passages 141 and 142, and mix with each other in the passage 4. The exhaust gas from the NO_x absorbing-reducing catalyst 7 is at a lean air-fuel ratio (an excess air ratio about 1.4) and contains a very small amount of NO_x , which passes through the NO_x absorbing-reducing catalyst 7. The exhaust gas from the three-way catalyst 5 is at a rich air-fuel ratio (an excess air ratio about 0.95) and contains a large amount of NH_3 . When these exhaust gases mix with each other, exhaust gas at a lean air-fuel ratio (an excess air ratio about 1.3) and containing a very small amount of NO_x and a large amount of NH_3 is formed. When this exhaust gas flows into the NH_3 adsorbing-denitrating catalyst 9 in the common exhaust gas passage 4, all the NO_x in the exhaust gas is reduced by reacting with NH_3 at the NH_3 adsorbing-denitrating catalyst, and a part of surplus NH_3 (i.e., NH_3 not used for reducing NO_x) is adsorbed by the NH_3 adsorbing-denitrating catalyst 9. Further, since the air-fuel ratio of the exhaust gas flowing into the NH_3 adsorbing-denitrating catalyst 9 is lean, the remaining part of NH_3 is purified on the NH_3 adsorbing-denitrating catalyst 9 and, thereby, the exhaust gas flowing through the NH_3 adsorbing-denitrating catalyst 9 does not contain NO_x nor NH_3 .

However, when the normal operation continues for a certain period, the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst 7 increases. Therefore, when the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst 7 increases to a predetermined value, a rich spike operation similar to that in the previous embodiments is performed on No. 2 through No. 4 cylinders in order to release NO_x from the NO_x absorbing-reducing catalyst 7.

Figs. 13 is a flowchart explaining the exhaust gas purifying operation in this embodiment. This operation is performed by a routine executed by the control circuit 30 at predetermined intervals.

The flowchart in Fig. 13 is substantially the same as the flowchart in Fig. 6. However, in Fig. 13, FL2 in steps 1301, 1309 and 1317 is a flag representing whether the rich spike operation is required for No. 2 through No. 4 cylinders and, FL2 = 1 means that the rich spike operation is not required. Further, CT2 in steps 1311 and 1313 is a counter for determining the length of the period for performing the rich spike operation. Similarly to CT in Fig. 6, the value of the CT2 is determined in accordance with the engine operating condition at step 1311. The value of CT2 corresponds to the time sufficient for reducing NO_x of the amount FNOX_0 absorbed in the NO_x absorbing-reducing catalyst 7 and, similarly to CT, is determined based on experiment. The values of CT is stored in the ROM of control circuit 30 in the form of a numerical table using the air intake amount Q and the speed N of the engine as parameters. In the operation of Fig. 13, the rich spike operation is performed on No. 2 through No. 4 cylinders for a period CT2 determined by the engine operating condition every time the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst 7 reaches the value FNOX_0 . Thus, NO_x is released and reduced every time the amount of NO_x in the NO_x absorbing-reducing catalyst 7 reaches the value FNOX_0 .

Fig. 14 is a flowchart similar to Fig. 7 which explains the fuel injection control operation in the present embodiment. This operation is performed by a routine executed by the control circuit 30 at a predetermined rotation angle of the crankshaft of the engine 1.

In Fig. 14, at step 1401, the excess air ratio λ_{1B} of the combustion (the excess air ratio of the air-fuel mixture obtained by the primary fuel injection) in No. 1 cylinder is set at λ_L , and the excess air ratio λ_{1A} of the exhaust gas leav-

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ing No. 1 cylinder (the excess air ratio of the exhaust gas after the additional fuel injection) is set at λ_R , respectively. λ_L is an excess air ratio where the amount of NO_x produced by the combustion becomes the maximum (for example, $\lambda_L = 1.2$), and λ_R is an excess air ratio where the amount of NH_3 produced by the three-way catalyst 5 becomes the maximum (for example, $\lambda_R = 0.95$). Further, at step 1401, the excess air ratios λ_{2B} and λ_{2A} of No. 2 through No. 4 cylinders are set at λ_{LL} and λ_{RR} , respectively. λ_{2B} is the excess air ratio of the combustion in No. 2 through No. 4 cylinders and λ_{LL} is an excess air ratio where NO_x produced by the combustion becomes the minimum (for example, $\lambda_{LL} = 1.4$). λ_{2A} is the excess air ratio of the exhaust gas leaving No. 2 through No. 4 cylinders, and λ_{RR} is an excess air ratio required for releasing NO_x from the NO_x absorbing-reducing catalyst 7. In this embodiment, λ_{RR} is set at an appropriate value lower than 1.0 ($\lambda_{RR} < 1.0$).

After setting excess air ratios of the cylinders at step 1401, the operation determines whether it is the primary fuel injection timing of No. 1 cylinder (step 1403), and whether it is the additional fuel injection timing of No. 1 cylinder (step 1407). If it is the timing for the primary fuel injection or the additional fuel injection of the No. 1 cylinder, the primary fuel injection and the additional fuel injection are performed at steps 1405 and 1409, respectively. By executing steps 1403 through 1409, the primary fuel injection of No. 1 cylinder is performed so that the excess air ratio of the combustion in No. 1 cylinder is always kept at λ_L , and the additional fuel injection of No. 1 cylinder is performed so that the excess air ratio of the exhaust gas leaving No. 1 cylinder is always kept at 0.95.

At steps 1411 through 1419, the primary fuel injection and the additional fuel injections of No. 2 through No. 4 cylinders are performed in the manner similar to steps 1403 through 1409. However, the additional fuel injections of No. 2 through No. 4 cylinders are performed only when the flag $FL2$ is set at 0. By executing steps 1411 through 1419, the excess air ratio of the combustion in No. 2 through No. 4 cylinders is always kept at λ_{LL} where the amount of NO_x produced by the combustion becomes small and, when rich spike operation is performed, the excess air ratio of the exhaust gas leaving No. 2 through No. 4 cylinders is adjusted to λ_{RR} by the additional fuel injection.

Although the NO_x absorbing-reducing catalyst 7 is disposed in the exhaust gas passage 141 in the embodiment in Fig. 12, the NO_x absorbing-reducing catalyst 7 may be disposed in the common exhaust gas passage 4 upstream of the NH_3 adsorbing-denitrating catalyst 9. An exhaust gas purifying operation the same as those in Figs. 13 and 14 can be performed also in this case.

Next, another embodiment of the present invention will be explained with reference to Fig. 15.

The embodiment in Fig. 15 is similar to the embodiment in Fig. 12 except that the NO_x absorbing-reducing catalyst 7 is disposed in the common exhaust gas passage 4 downstream of the NH_3 adsorbing-denitrating catalyst 9. Namely, in this embodiment, NH_3 adsorbing-denitrating catalyst 9 mainly purifies NO_x in the exhaust gas, and the NO_x absorbing-reducing catalyst 7 downstream of the NH_3 adsorbing-denitrating catalyst 9 purifies only a small amount of NO_x which has passed through the NH_3 adsorbing-denitrating catalyst 9 without being reduced.

In this embodiment, the additional fuel injection of No. 1 cylinder is always performed to produce a large amount of NH_3 at the three-way catalyst 5. The exhaust gas flowing through the three-way catalyst 5 mixes with a lean air-fuel ratio exhaust gas from No. 2 through No. 4 cylinders and forms an exhaust gas with a lean air-fuel ratio as a whole. When this lean air-fuel ratio exhaust gas containing NH_3 flows into NH_3 adsorbing-denitrating catalyst 9, NO_x in the exhaust gas reacts with NH_3 on the NH_3 adsorbing-denitrating catalyst 9 and is reduced to N_2 . In this case, a very small amount of NO_x may pass through the NH_3 adsorbing-denitrating catalyst 9 without being reduced. However, even if NO_x passes through the NH_3 adsorbing-denitrating catalyst 9, the NO_x passing through the catalyst 9 is absorbed by the NO_x absorbing-reducing catalyst 7 downstream of the catalyst 9 and removed from the exhaust gas. Similarly to the embodiment in Fig. 12, the rich spike operation is performed on No. 2 through No. 4 cylinders when the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst 7 reaches a predetermined value in this embodiment, in order to prevent the NO_x absorbing-reducing catalyst 7 from being saturated with the absorbed NO_x .

Since the exhaust gas purifying operation in this embodiment is the same as those in Figs. 13 and 14, a detailed explanation is omitted. However, ANOX in steps 1303 and 1305 in Fig. 13 represents the amount of NO_x passing through the NH_3 adsorbing-denitrating catalyst 9 without being reduced and flows into the NO_x absorbing-reducing catalyst 7 per unit time instead of the whole amount of NO_x produced by the engine per unit time. Therefore, the values of ANOX in this embodiment are far smaller than the values used in the embodiment in Fig. 12. The values of ANOX are preferably determined based on experiment also in this embodiment.

Next, another embodiment of the present invention will be explained with reference to Fig. 16.

The embodiment in Fig. 16 has an arrangement similar to that of Fig. 15, except that the NO_x absorbing-reducing catalyst 7 in Fig. 15 is omitted.

In this embodiment, either of the following two types of the exhaust gas purifying operations can be performed.

The first type of the exhaust gas purifying operation always performs the additional fuel injection of No. 1 cylinder in order to produce NH_3 at the three-way catalyst 5, and operates No. 2 through No. 4 cylinders at the excess air ratio where the amount of NO_x produced by the combustion becomes small. In the first type of the exhaust gas purifying operation, thus the lean air-fuel ratio exhaust gas containing both NO_x and NH_3 is always supplied to the NH_3 adsorbing-denitrating catalyst 9, and the NO_x is reduced at the NH_3 adsorbing-denitrating catalyst 9 by reacting with NH_3 . In this

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case, the primary fuel injection amount of No. 1 cylinder is set at a value so that the excess air ratio of the combustion becomes a value where the amount of NO_x produced by the combustion becomes the maximum (i.e., $\lambda = 1.2$), and the additional fuel injection amount of No. 1 cylinder is set at a value so that the excess air ratio of the exhaust gas leaving No. 1 cylinder becomes a value where the amount of NH_3 produced by the three-way catalyst 5 becomes the maximum (i.e., $\lambda = 0.95$). The rich spike operation is not performed on No. 2 through No. 4 cylinders.

In contrast to the above, in the second type of the exhaust gas purifying operation all the cylinders are operated at a lean air-fuel ratio during the normal operation of the engine, and NO_x in the exhaust gas is purified at the NH_3 adsorbing-denitrating catalyst 9 using NH_3 stored therein. Further, when the amount of NH_3 stored in the NH_3 adsorbing-denitrating catalyst 9 decreases to a predetermined value, the rich spike operation of No. 1 cylinder is performed in order to replenish the NH_3 adsorbing-denitrating catalyst 9 with NH_3 .

Fig. 17 is a flowchart explaining the exhaust gas purifying operation of the second type. This operation is performed by a routine executed by the control circuit 30 at predetermined intervals.

In this operation, the amount INH_3 of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 is calculated by the method same as that explained in Fig. 11 (steps 1703 and 1705). Then, if the amount INH_3 has decreased to a predetermined value I_0 , the operation sets a lean operation flag FL1 to 0. FL1 is a lean operation flag of No. 1 cylinder. Further, the operation performs the additional fuel injection of No. 1 cylinder for a predetermined period CTG , in order to increase the amount of NH_3 in the catalyst 9 to the value IFUL (steps 1707 through 1719). IFUL is, as explained before, the value near the saturation amount of NH_3 of the NH_3 adsorbing-denitrating catalyst 9.

Fig. 18 is a flowchart explaining the fuel injection control operation of the present embodiment. This operation is performed by a routine executed by the control circuit 30 at a predetermined rotation angle of the crankshaft of the engine. In this operation, the excess air ratio λ_{2B} of the combustion in No. 2 through No. 4 cylinders is always set at λ_{LL} ($\lambda_{LL} = 1.4$) where the amount of NO_x produced by the combustion becomes the minimum (step 1801). The excess air ratio λ_{1B} of the combustion in No. 1 cylinder is determined in accordance with the value of the lean operation flag FL1 . Namely, if $\text{FL1} = 1$ at step 1803, i.e., if the rich spike operation is not required, λ_{1B} is set at λ_{LL} at step 1805, and if $\text{FL1} = 0$, i.e., if the rich spike operation is required, λ_{1B} is set at λ_L ($\lambda_L = 1.2$) where the amount of NO_x produced by the combustion becomes the maximum (step 1807). Further, at step 1809, the operation determines whether it is the timing for the primary fuel injection of any one of the cylinders. If it is the timing, the primary fuel injection is performed on the corresponding cylinder at step 1811. If it is not the timing at step 1809, the operation determines whether the flag FL1 is set at 1 at step 1813, and if $\text{FL1} = 1$, performs the additional fuel injection of No. 1 cylinder at the timing for the additional fuel injection of No. 1 cylinder (steps 1815 and 1817).

By the operations in Figs. 17 and 18, the rich spike operation of No. 1 cylinder is performed when the amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 decreases to a predetermined value and, thereby, the amount of NH_3 in the catalyst 9 increases to the value IFUL near the saturating amount by the rich spike operation.

Next, another embodiment is explained with reference to Fig. 19. Similarly to the embodiment in Fig. 16, the embodiment in Fig. 19 performs the exhaust gas purifying operation using only the three-way catalyst 5 and the NH_3 adsorbing-denitrating catalyst 9. However, in this embodiment, the exhaust gas from No. 2 cylinder can be directed to either of the exhaust gas passage 143 (the three-way catalyst 5 side) and exhaust gas passage 141 in accordance with the amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9.

Namely, in Fig. 19, the exhaust port of No. 1 cylinder is directly connected to the exhaust gas passage 143, and the exhaust port of No. 2 cylinder is connected to an exhaust gas passage 171. The exhaust gas passage 171 of No. 2 cylinder diverges into branch exhaust gas passages 172 and 173. The branch exhaust gas passage 172 is connected to the exhaust gas passage 141, and the branch exhaust gas passage 173 is connected to the exhaust gas passage 143 upstream of the three-way catalyst 5. A switching valve 175 is provided on the exhaust gas passage 171 at the point where the branch passages 172 and 173 diverges. The switching valve 175 is provided with an appropriate actuator 175a, such as a solenoid actuator or a vacuum actuator, and takes a first position where the exhaust gas passage 171 is connected to the exhaust gas purifying catalyst 172 (i.e., the No. 3 and No. 4 cylinders side position) and a second position where the exhaust gas passage 171 is connected to the exhaust gas passage 173 (i.e., the three-way catalyst 5 side position) in response to a control signal from the control circuit 30. Therefore, the exhaust gas from No. 2 cylinder can be directed either to the three-way catalyst 5 or the exhaust gas passage 141. Thus, the amount of NO_x supplied to the three-way catalyst 5 can be changed by switching the flow of the exhaust gas between the three-way catalyst side and the No. 3 and No. 4 cylinders side. Therefore, the amount of NH_3 produced at the three-way catalyst 5 can be changed in accordance with the operating condition of the engine.

In this embodiment, the excess air ratios of the combustion in No. 3 and No. 4 cylinders (λ_{3B} , λ_{4B} , respectively) are set at λ_{LL} ($\lambda_{LL} = 1.4$) where the amount of NO_x produced by the combustion becomes the minimum, and the additional fuel injection is not performed on No. 3 and No. 4 cylinders. The amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 in this embodiment is controlled by switching the valve 175. Namely, when the amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 becomes smaller than a predetermined lower limit I_1 , the switching valve 175 is switched to the three-way catalyst side position to supply the exhaust gases from both No. 1 and No. 2 cylinders to the

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three-way catalyst 5. In this case, the excess air ratios of the primary fuel injections of No. 1 and No. 2 cylinders (λ_{1B} , λ_{2B} , respectively) are set at λ_L ($\lambda_L = 1.2$) where the amount of NO_x produced by the combustion becomes the maximum. Further, the additional fuel injection is performed on No. 1 and No. 2 cylinder to adjust the excess air ratio of the exhaust gas leaving these cylinders to λ_R ($\lambda_R = 0.95$) where the amount of NH_3 produced at the three-way catalyst 5 becomes the maximum. Therefore, NO_x produced by No. 1 and No. 2 cylinders is converted into NH_3 at the three-way catalyst 5 and the amount of NH_3 produced by the three-way catalyst 5 increases. This large amount of NH_3 is supplied to the NH_3 adsorbing-denitrating catalyst 9 disposed downstream of the three-way catalyst 5, and the amount of NH_3 adsorbed by the NH_3 adsorbing-denitrating catalyst 9 increases in a short time.

When the amount of NO_x held in the NH_3 adsorbing-denitrating catalyst 9 is larger than the lower limit I_1 , but smaller than an upper limit IFUL near the saturating amount, the switching valve 175 is switched to the No. 3 and No. 4 cylinders side position to supply the exhaust gas only from No. 1 cylinder to the three-way catalyst 5. In this case, the excess air ratio λ_{2B} of No. 2 cylinder is set at λ_{LL} and the additional fuel injection of the No. 2 cylinder is terminated. Therefore, since only NO_x in the exhaust gas from No. 1 cylinder is converted into NH_3 at the three-way catalyst 5, the amount of NH_3 supplied to the NH_3 adsorbing-denitrating catalyst 9 becomes smaller and, thereby, the amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 increases (or decreases) slowly.

Further, when the amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 increases to the upper limit IFUL , the additional fuel injection of No. 1 cylinder is terminated, and the excess air ratio λ_{1B} of the primary fuel injection of No. 1 cylinder is set to λ_{LL} where the amount of NO_x produced by the combustion becomes the minimum. In this case, since no NH_3 is produced at the three-way catalyst 5, the amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 decreases in a relatively short time.

Fig. 20 is a flowchart explaining the exhaust gas purifying operation of the present embodiment. This operation is performed by a routine executed by the control circuit 30 at predetermined intervals.

In Fig. 20, at step 2001, the operation determines whether the amount INH_3 of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 reaches the predetermined value IFUL (which is near the saturating amount of NH_3). If the amount INH_3 has reached IFUL , i.e., if $\text{INH}_3 \geq \text{IFUL}$ at step 2001, the operation sets the value of a flag FR to 0 at step 2003, and calculates the amount BNOX of NO_x produced by the engine per unit time, based on the engine operating condition (the air intake amount Q and the speed N of the engine). As explained later, when the value of the flag FR is set to 0, the excess air ratio of the primary fuel injection of all the cylinders No. 1 through No. 4 is set at λ_{LL} , and the additional fuel injections of No. 1 and No. 2 cylinders are stopped by the fuel injection control operation performed by the control circuit 30 separately.

In this embodiment, the value BNOX is different from ANOX in the previous embodiments in that it represents the amount of NO_x produced by one cylinder per unit time, and obtained previously by experiment. The values of BNOX are stored in the ROM of the control circuit 30 in the form of a numerical table using Q and N as parameters.

At step 2007, the amount INH_3 of NH_3 stored in the NH_3 adsorbing-denitrating catalyst 9 is calculated by $\text{INH}_3 = \text{INH}_3 - K \times 4 \times \text{BNOX}$. Namely, since NH_3 in the NH_3 adsorbing-denitrating catalyst 9 is used for reducing NO_x produced by four cylinders, the amount of NO_x in the NH_3 adsorbing-denitrating catalyst 9 decreases ($K \times 4 \times \text{BNOX}$) per unit time.

If $\text{INH}_3 < \text{IFUL}$ at step 2001, the operation proceeds to step 2009 to determine whether the amount INH_3 is smaller than the lower limit I_1 . If $\text{INH}_3 > I_1$ at step 2009, the operation sets the value of the flag FR to 1 at step 2011, and switches the switching valve 175 to the No. 3 and No. 4 side position at step 2013. By this operation, only the exhaust gas from No. 1 cylinder is supplied to the three-way catalyst 5. At step 2015, the operation calculates the amount BNOX of NO_x produced per one cylinder of No. 2 through No. 4 cylinders. Further, the operation calculates the amount BNH_3 of NH_3 produced by the three-way catalyst 5 per unit time based on the operating condition (air intake amount Q and speed N) of the engine 1. When the value of the flag FR is set to 1, the excess air ratio λ_{1B} of the primary fuel injection of No. 1 cylinder is set to λ_L and the additional fuel injection is performed on No. 1 cylinder. In this case, the excess air ratio of the primary fuel injection of No. 2 cylinder is set to λ_{LL} , i.e., the excess air ratio the same as that in No. 3 and No. 4 cylinders, and the additional fuel injection of No. 2 cylinder is stopped. Further, at step 2019, the amount INH_3 is calculated by $\text{INH}_3 = \text{INH}_3 + \text{BNH}_3 - K \times 3 \times \text{BNOX}$. Namely, in this case, the amount INH_3 increases by the amount BNH_3 of NH_3 produced by the three-way catalyst 5, and decreases by the amount ($K \times 3 \times \text{BNOX}$) required for reducing NO_x produced by three cylinders.

If $\text{INH}_3 \leq I_1$ at step 2009, the operation sets the value of the flag FR to 2 at step 2021, and switches the switching valve 175 to the three-way catalyst 5 side. Thus, the exhaust gases from both No. 1 and No. 2 cylinders are supplied to three-way catalyst 5. Further, when the value of the flag FR is set at 2, the excess air ratio λ_{2B} of No. 2 cylinder is set to λ_L , and the additional fuel injection is also performed on No. 2 cylinder.

Further, the amount INH_3 is calculated at steps 2025 through 2029 in the manner similar to that in steps 2015 through 2019. However, INH_3 is calculated by $\text{INH}_3 = \text{INH}_3 + 2 \times \text{BNH}_3 - K \times 2 \times \text{BNOX}$ in this case. Namely, the amount INH_3 increases by the amount of NH_3 produced from NO_x supplied by two cylinders (No. 1 and No. 2 cylinders) and decreases by the amount required to reduce NO_x contained in the exhaust gas from two cylinders (No. 3 and No.

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4 cylinders).

Figs. 21 and 22 are a flowchart explaining the fuel injection control operation in this embodiment. This operation is performed by a routine executed by the control circuit 30 at a predetermined rotation angle of the crankshaft.

In Fig. 21, steps 2101 through 2125 represent the control operation of the primary fuel injection of the respective cylinders. Namely, the amounts of the primary fuel injection of No. 3 and No. 4 cylinders are set at step 2101 so that the excess air ratios λ_{3B} and λ_{4B} of the combustion in the No. 3 and No. 4 cylinders become λ_{LL} , and the primary fuel injections of No. 3 and No. 4 cylinders are performed at steps 2103 and 2105 at the fuel injection timing of these cylinders.

The excess air ratio λ_{1B} of the primary fuel injection of No. 1 cylinder is set in accordance with whether the value of the flag FR is 0, and the primary fuel injection of No. 1 cylinder is performed when it becomes the fuel injection timing, at steps 2107 through 2115. The excess air ratio λ_{1B} of No. 1 cylinder is set to λ_L when the value of FR is 1 or 2 (step 2109), and to λ_{LL} when the value of FR is 0 (step 2111).

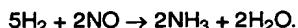
Further, the excess air ratio λ_{2B} of the primary fuel injection of No. 2 cylinder is set in accordance with whether the value of the flag FR is 1, and the primary fuel injection of No. 2 cylinder is performed when it becomes the fuel injection timing at steps 2117 through 2125. The excess air ratio λ_{2B} of No. 2 cylinder is set to λ_{LL} when the value of FR is 1 (step 2119), and to λ_L when the value of FR is 2 (step 2121).

After setting the excess air ratios of the respective cylinders, the control of the additional fuel injections of No. 1 and No. 2 cylinders are performed at steps 2127 through 2141. Namely, it is determined whether the value of the flag FR is 0 at step 2127 and, if FR = 0, since the additional fuel injections are not required for No. 1 and No. 2 cylinders, the operation terminates immediately. On the other hand, if FR ≠ 0 at step 2127 (i.e., if FR is 1 or 2), since the additional fuel injection is required on the No. 1 cylinder, the amount of the additional fuel injection of No. 1 cylinder is determined at step 2129 in such a manner that the excess air ratio λ_{1A} of the exhaust gas leaving No. 1 cylinder becomes λ_R . The additional fuel injection is then performed at the additional fuel injection timing (steps 2131 and 2133). Further, the operation determines whether the value of the flag FR is 1 at step 2135 and, if FR = 1 (i.e., if the additional fuel injection is not required for No. 2 cylinder), the operation terminates immediately. If FR ≠ 1 at step 2135 (i.e., if FR = 2), since this means that the additional fuel injection is required for No. 2 cylinder, the operation sets the amount of additional fuel injection at step 2137 so that the excess air ratio λ_{2A} of the exhaust gas leaving No. 2 cylinder becomes λ_R , and performs additional fuel injection of No. 2 cylinder at steps 2139 and 2141.

According to the present embodiment, since the amount of NH_3 produced at the three-way catalyst 5 is controlled in such a manner that the amount of NH_3 held in the NH_3 adsorbing-denitrating catalyst 9 is always kept within a predetermined range, the shortage of NH_3 on the catalyst 9 or the saturation thereof with NH_3 determining operation not occur. Therefore, NO_x in the exhaust gas is purified with high efficiency in this embodiment.

Next, other embodiments of the present invention will be explained. The previous embodiments in Figs. 1, 8 through 10, 12, 15, 16 and 19 use the three-way catalyst 5 as the NH_3 conversion means. However, in the embodiments explained hereinafter, an NO_x absorbing-reducing catalyst is used instead of three-way catalyst as NH_3 conversion means.

As explained before, the NO_x absorbing-reducing catalyst absorbs NO_x in the exhaust gas when the air-fuel ratio of the exhaust gas is lean, and releases and reduces the absorbed NO_x when the air-fuel ratio of the exhaust gas becomes rich. However, it was found that the NO_x absorbing-reducing catalyst also converts NO_x into NH_3 when the air-fuel ratio of the exhaust gas is rich by the reaction the same as that of the three-way catalyst, i.e.,



In this case, it was also found that both of the NO_x in the exhaust gas and the NO_x absorbed in the NO_x absorbing-reducing catalyst are converted into NH_3 . Therefore, when the NO_x absorbing-reducing catalyst is used as the NH_3 conversion means, since the NO_x absorbed in the NO_x absorbing-reducing catalyst in addition to the NO_x in the exhaust gas can be used for producing NH_3 , the amount of the produced NO_x becomes larger compared to the amount of NO_x produced by the three-way catalyst provided other conditions are the same.

Figs. 23 through 27 show the general configurations of embodiments of the exhaust gas purification device according to the present invention when the NO_x absorbing-reducing catalysts are used as NH_3 conversion means. Figs. 23 through 26 show the embodiments where exhaust gases from all the cylinders of the engine flow through the NO_x absorbing-reducing catalyst used as the NH_3 conversion means, while Fig. 27 shows the embodiment where only the exhaust gas from the specific cylinder flows through the same. Reference numerals in Figs. 23 through 27 which are the same as those in Figs. 1, 8 through 10, 12, 15, 16 and 19 designate similar elements.

First, the embodiment in Fig. 23 will be explained.

In this embodiment, No. 1 and No. 4 cylinders are connected to a branch exhaust gas passage 4a by an exhaust manifold 133a, and No. 2 and No. 3 cylinders are connected to another branch exhaust gas passage 4b by an exhaust manifold 133b. The branch exhaust gas passages 4a and 4b merges each other to form a common exhaust gas passage 4 at downstream thereof. A NO_x absorbing-reducing catalyst is disposed in each of the branch exhaust gas pas-

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sage 4a and 4b in this embodiment. Since these NO_x absorbing-reducing catalyst act as NH_3 conversion means, these NO_x absorbing-reducing catalysts are designated by numerals 70a and 70b (or 70) in Figs. 23 through 27 to distinguish them from the NO_x absorbing-reducing catalyst mainly acting as the purification means. In the common exhaust gas passage 4, a NO_x absorbing-reducing catalyst 7 which mainly acts as the purification means and the NH_3 adsorbing-denitrating catalyst 9 are disposed in this order from the upstream end.

In this embodiment, all the cylinders are always operated at the same excess air ratio. Namely, though two groups of cylinders are formed, and a branch exhaust gas passage is connected to each group of cylinders in order to decrease the exhaust back pressure by avoiding interference of exhaust gases from the respective cylinders, the configuration of the embodiment in Fig. 23 is substantially the same as that in Fig. 1 since the NH_3 conversion means (the NO_x absorbing-reducing catalysts 70a and 70b) are disposed in both branch exhaust gas passages 4a and 4b.

Further, the exhaust gas purifying operation of the present embodiment is the same as the operation of the embodiment in Fig. 1, i.e., the operations in Figs. 6 and 7 are also performed in this embodiment. Namely, all the cylinders of the engine 1 are operated at a lean air-fuel ratio during the normal operation. In the normal operation, the upstream NO_x absorbing-reducing catalysts 70a and 70b, as well as the downstream NO_x absorbing-reducing catalyst 7 absorb NO_x in the exhaust gas. When the amount of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 increased to a predetermined value, the rich spike operation is performed on all cylinders. Therefore, a rich air-fuel ratio exhaust gas containing a relatively large amount of NO_x flows into the upstream NO_x absorbing-reducing catalysts 70a, 70b acting as the NH_3 conversion means. When the rich air-fuel ratio exhaust gas is supplied to the upstream NO_x absorbing-reducing catalysts 70a and 70b, NO_x absorbed in the catalysts 70a and 70b are released. This released NO_x , as well as NO_x contained in the exhaust gas from the engine, is converted into NH_3 at the upstream NO_x absorbing-reducing catalysts 70a and 70b, and a large amount of NH_3 is produced. Thus, a rich air-fuel ratio exhaust gas containing a large amount of NH_3 flows into the downstream NO_x absorbing-reducing catalyst 7 and, thereby, NO_x is released from the catalyst 7 and reduced to N_2 by reacting with NH_3 in the exhaust gas.

In the operation in Fig. 6, it is assumed that the upstream NO_x absorbing-reducing catalysts 70a performs only the function as the NH_3 conversion means, i.e., the function exactly the same as the three-way catalyst 5 in Fig. 1. Therefore, the absorbing and releasing of NO_x by the NO_x absorbing-reducing catalysts 70a and 70b is ignored. However, since the upstream NO_x absorbing-reducing catalysts 70a and 70b also absorb NO_x in the exhaust gas during the normal operation, the actual amount of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 becomes smaller in this embodiment compared to the embodiment in Fig. 1. Therefore, it is preferable to take the absorbing and releasing operation of the upstream NO_x absorbing-reducing catalysts 70a and 70b into consideration. The exhaust gas purifying operation which takes the absorbing and releasing operation of the upstream NO_x absorbing-reducing catalysts into consideration will be explained later (Fig. 28).

Fig. 24 shows an embodiment where the NO_x absorbing-reducing catalysts 70a and 70b are used as NH_3 conversion means, and the NH_3 adsorbing-denitrating catalyst 9 and the downstream NO_x absorbing-reducing catalyst 7 are disposed in the exhaust gas passage 4 in this order from the upstream end. As can be seen from Fig. 24 and Fig. 8, the embodiment in Fig. 24 is substantially the same as the embodiment in Fig. 8. Since the exhaust gas purifying operation of the embodiment in Fig. 24 is also the same as the operation in the embodiment in Fig. 8, a detailed explanation is omitted.

Fig. 25 shows an embodiment where only the downstream NO_x absorbing-reducing catalyst 7 is provided on the exhaust gas passage 4 downstream of the upstream NO_x absorbing-reducing catalysts 70a and 70b. Fig. 26 shows an embodiment where only the NH_3 adsorbing-denitrating catalyst 9 is disposed in the exhaust gas passage 4 downstream of the NO_x absorbing-reducing catalysts 70a and 70b. The embodiments in Figs. 25 and 26 are substantially the same as the embodiments in Figs. 9 and 10, respectively. The exhaust gas purifying operations in the embodiments in Figs. 25 and 26 are also the same as those in the embodiments in Figs. 9 and 10.

Fig. 27 shows an embodiment in which only the exhaust gas from the specific cylinder is supplied to the NO_x absorbing-reducing catalyst 70 which acts as the NH_3 conversion means. This embodiment only replaces the three-way catalyst 5 in the embodiment in Fig. 12 with the NO_x absorbing-reducing catalyst 70 and substantially the same as the embodiment in Fig. 12. The exhaust gas purifying operation of the embodiment in Fig. 27 is also exactly the same as the operation in the embodiment in Fig. 12. Further, though not shown by drawings, it is possible to replace the three-way catalyst 5 in the embodiments in Figs. 15, 16 and 19 with the NO_x absorbing-reducing catalyst 7, and the exhaust gas purifying operations do not change even if the three-way catalyst 5 is replaced with the NO_x absorbing-reducing catalyst 7 in the embodiments in Figs. 15, 16 and 19.

Next, another embodiment of the exhaust gas purifying operation where the NO_x absorbing-reducing catalyst is used as the NH_3 conversion means will be explained. In the embodiments in Figs. 23 through 27, though the NO_x absorbing-reducing catalysts are used as the NH_3 conversion means, the exhaust gas purifying operations are the exactly the same as the exhaust gas purifying operations where the three-way catalysts are used as the NH_3 conversion means. However, though the three-way catalyst only allows NO_x to pass through, the NO_x absorbing-reducing catalyst absorbs NO_x in the exhaust gas when the exhaust gas is at a lean air-fuel ratio. In this embodiment, this NO_x

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absorbing and releasing operation is utilized effectively even though the NO_x absorbing-reducing catalyst is used as the NH_3 conversion means.

Fig. 28 is a flowchart explaining the embodiment of the exhaust gas purifying operation. Although this exhaust gas purifying operation can be performed in any embodiment of Fig. 23 through 27, the case in Fig. 23 is considered for the purpose of explanation.

5 The operation in Fig. 28 is performed by a routine executed by the control circuit 30 at predetermined intervals.

Similarly to the operation in Fig. 6, in this operation, the amount of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 is calculated and, when the calculated amount of NO_x increases to a predetermined value, the rich spike operation is performed, to produce NH_3 , by the upstream NO_x absorbing-reducing catalysts 70a and 70b. 10 However, since the upstream NO_x absorbing-reducing catalysts 70a and 70b also absorb NO_x in the exhaust gas during the normal operation, the amount of NO_x in the exhaust gas flowing into the downstream NO_x absorbing-reducing catalyst 7 is very small compared to that in the embodiment in Fig. 1. However, the upstream NO_x absorbing-reducing catalysts 70a and 70b in this embodiment are relatively small in size, and the capacity for absorbing NO_x thereof is relatively small. As is well known, when the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst increases, 15 the amount of NO_x passing through the catalyst without being absorbed gradually increases as the amount of the absorbed NO_x approaches to the saturating amount. Therefore, as the amount of the absorbed NO_x in the NO_x absorbing-reducing catalysts 70a and 70b increases and approaches to the saturating amount, the amount of NO_x absorbed by the downstream NO_x absorbing-reducing catalyst 7 gradually increases. In this embodiment, it is assumed that the amount of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 does not increase when the amount of 20 absorbed NO_x in the upstream NO_x absorbing-reducing catalysts 70a and 70b is small, since it is thought that NO_x in the exhaust gas does not pass through the upstream catalysts 70a and 70b when the amount of the NO_x absorbed therein is small. Further, it is also assumed that a part of NO_x starts to pass through the upstream NO_x absorbing-reducing catalysts 70a and 70b when the amount of the absorbed NO_x in the upstream catalysts 70a and 70b reaches 25 a predetermined value and the amount of NO_x absorbed in the downstream catalyst 7 also starts to increase. Therefore, in this embodiment, the time required for the NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 to increase to the upper limit value is longer compared to that in the embodiment in Fig. 1. Therefore, by considering the amount of NO_x absorbed by the upstream NO_x absorbing-reducing catalysts 70a and 70b, the interval between the rich spike operation of the engine can be set longer in this embodiment.

30 The flowchart in Fig. 28 will be explained briefly. The flowchart in Fig. 28 is similar to the flowchart in Fig. 6 except that steps 2821 through 2825 are added to Fig. 6.

In this operation, the amount ANOX of NO_x produced by the engine per unit time during the lean air-fuel ratio operation (step 2801) is calculated (step 2803) in the manner the same as step 603 in Fig. 6. At step 2805 the value of the counter F1NOX is increased by ANOX . The counter F1NOX represents the amount of NO_x absorbed in the upstream NO_x absorbing-reducing catalyst 70a and 70b. At step 2807 the operation determines whether the value of the counter 35 F1NOX reaches a predetermined value F1NOX_0 . F1NOX_0 is the amount of NO_x absorbed in the upstream NO_x absorbing-reducing catalysts 70a and 70b where NO_x in the exhaust gas passes through the catalysts 70a and 70b due to increase in the amount of NO_x absorbed therein. The value of F1NOX_0 is set at a value about the same as FNOX_0 in Fig. 6 (for example, about 70% of the saturating amount). If the amount F1NOX has not reached the value F1NOX_0 at step 2807, the operation immediately terminates. In this case, the value of the counter F2NOX which represents the 40 amount of the NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 is not increased.

If the value of F1NOX has reached F1NOX_0 at step 2807, since this means that a part of NO_x flowing into the upstream NO_x absorbing-reducing catalysts 70a and 70b passes through without being absorbed by the upstream catalysts 70a and 70b, the operation calculates the amount A2NOX of NO_x passing through the upstream catalysts 70a and 70b per unit time at step 2811. The value of A2NOX becomes larger as the amount of NO_x absorbed in the NO_x absorbing-reducing catalysts 70a and 70b approaches to the saturating amount. Further, the value of A2NOX increases 45 as the amount of NO_x produced by the engine per unit time increases. In this embodiment, the amount A2NOX is previously measured under various conditions of the amount F1NOX of NO_x absorbed in the NO_x absorbing-reducing catalysts 70a, 70b, and the amount ANOX of NO_x produced by the engine per unit time. The measured result is stored in the ROM of the control circuit 30 in the form of a numerical table using F1NOX and ANOX as parameters. The value of 50 A2NOX is determined from the F1NOX and ANOX using this numerical table at step 2821. Since the amount A2NOX of NO_x passes through the upstream NO_x absorbing-reducing catalyst 70a and 70b and is absorbed by the downstream NO_x absorbing-reducing catalyst 7, the amount of NO_x held in the downstream NO_x absorbing-reducing catalyst increases A2NOX per unit time. Therefore, the value of the counter F2NOX which represents the amount of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 is increased by ANOX at step 2823. In this operation 55 when the value of F2NOX reaches a predetermined value F2NOX_0 at step 2825, the rich spike operation of the cylinders starts at steps 2809 and 2811.

Step 2809 (the resetting of the flag FL), step 2811 (the setting of the rich spike operation period CT) are the operation exactly the same as steps 609 and 611 in Fig. 6, respectively. Further, steps 2813 through 2819 are the operations

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same as steps 613 through 619. Therefore, the detailed explanation of these steps is omitted here.

Fig. 29 is a diagram illustrating the change in the amounts of NO_x absorbed in the upstream catalysts 70a, 70b and the downstream catalyst 7 during the exhaust gas purifying operation of the present embodiment. In Fig. 29, the curve A represents the amount $F1\text{NOX}$ of NO_x absorbed in the upstream NO_x absorbing-reducing catalysts 70a and 70b, and the curve B represents the amount $F2\text{NOX}$ of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7. As can be seen from the curve A in Fig. 29, when the amount $F1\text{NOX}$ increases and reaches the value $F1\text{NOX}_0$ (the time point I in Fig. 29), a part of NO_x starts to pass through the upstream catalysts 70a and 70b. Therefore, the amount $F2\text{NOX}$ of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 starts to increase (the time point I in Fig. 29). The amount of NO_x passing through the upstream NO_x absorbing-reducing catalysts 70a, 70b increases as the amount $F1\text{NOX}$ increases, and after the amount $F1\text{NOX}$ has reached the saturating amount of the catalysts 70a, 70b, all of the NO_x produced by the engine passes through the upstream catalysts 70a, 70b and is absorbed by the downstream NO_x absorbing-reducing catalyst 7. Therefore, the rate of the increase in the amount $F2\text{NOX}$ of NO_x absorbed in the downstream NO_x absorbing-reducing catalyst becomes larger as time elapses. When the amount $F2\text{NOX}$ of the NO_x absorbed in the downstream NO_x absorbing-reducing catalyst 7 reaches the amount of $F2\text{NOX}_0$, the rich spike operation is performed by the operation shown in Fig. 28 (the time point II in Fig. 29) and, thereby, all the NO_x absorbed in the upstream catalysts 70a, 70b and the downstream catalyst 7 is released and reduced. Therefore, the amounts $F1\text{NOX}$ and $F2\text{NOX}$ become 0 after the rich spike operation has completed.

As explained above, according to the present embodiment, since the timing for performing the rich spike operation is determined taking the NO_x absorbing capability of the upstream NO_x absorbing-reducing catalyst 70a and 70b (i.e., the NH_3 conversion means), the interval between the rich spike operation can be set longer compared to the case where the three-way catalyst is used as the NH_3 conversion means.

In an exhaust gas purification device, a three-way catalyst, an NO_x absorbing-reducing catalyst and an NH_3 adsorbing-denitrating catalyst are disposed in an exhaust gas passage of the internal combustion engine. The engine is provided with direct cylinder injection valves which inject fuel directly into the respective cylinders. A control circuit controls the amount of fuel injected from the injection valve so that the air-fuel ratio of the combustion in the cylinders becomes a lean air-fuel ratio during the normal operation of the engine. Therefore, a lean air-fuel ratio exhaust gas is discharged from the cylinders during the normal operation and NO_x in the exhaust gas is absorbed by the NO_x absorbing-reducing catalyst. When the amount of NO_x absorbed in the NO_x absorbing-reducing catalyst increases to a predetermined level, the control circuit performs an additional fuel injection during the expansion stroke or exhaust stroke of cylinders in order to adjust the air-fuel ratio of the exhaust gas leaving the cylinders to a rich air-fuel ratio. The rich air-fuel ratio exhaust gas leaving the cylinders flows into the three-way catalyst and NO_x in the exhaust gas is converted into NH_3 at the three-way catalyst. When the rich air-fuel ratio exhaust gas flows through the NO_x absorbing-reducing catalyst, NO_x is released from the NO_x absorbing-reducing catalyst and is reduced to N_2 by NH_3 in the exhaust gas.

35 Claims

1. An exhaust gas purification device for an internal combustion engine, said engine being provided with a direct cylinder injection valve for injecting fuel directly into the cylinder thereof and is capable of operating on a lean air-fuel ratio combustion in the cylinder, said device comprising:

40 exhaust gas air-fuel ratio adjusting means for adjusting the air-fuel ratio of the lean air-fuel ratio exhaust gas produced by the lean air-fuel ratio combustion in the cylinder to a rich air-fuel ratio by injecting fuel into the cylinder from the direct cylinder injection valve during an expansion stroke or an exhaust stroke of the cylinder, NH_3 conversion means disposed in an exhaust gas passage through which the exhaust gas after its air-fuel ratio is adjusted flows and for producing NH_3 by converting at least a part of NO_x contained in the exhaust gas to NH_3 ; and

45 NH_3 purification means disposed in an exhaust gas passage into which the exhaust gas from the NH_3 conversion means flows and for purifying both NO_x and NH_3 in the exhaust gas by reacting NO_x with NH_3 in the exhaust gas.

50 2. An exhaust gas purification device as set forth in claim 1, wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH_3 produced by the NH_3 conversion means by changing the length of the period for adjusting the air-fuel ratio of the exhaust gas to a rich air-fuel ratio.

55 3. An exhaust gas purification device as set forth in claim 1, wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH_3 produced by the NH_3 conversion means by changing the number of cylinders in which the direct fuel injection, during the expansion or exhaust strokes, is performed.

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4. An exhaust gas purification device as set forth in claim 1, wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH₃ produced by the NH₃ conversion means by changing the value of the air-fuel ratio of the exhaust gas after it is adjusted.
5. An exhaust gas purification device as set forth in one of claims 1 through 4, wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH₃ produced by the NH₃ conversion means in accordance with the operating condition of the engine.
6. An exhaust gas purification device as set forth in claim 1, wherein the purification means comprises an NH₃ adsorbing-denitrating catalyst which adsorbs NH₃ in the exhaust gas and reduces NO_x in the exhaust gas using the NH₃ it has adsorbed or the NH₃ in the exhaust gas.
7. An exhaust gas purification device as set forth in claim 1, wherein the purification means comprises an NO_x absorbing-reducing catalyst which absorbs NO_x in the exhaust gas when the exhaust gas is at a lean air-fuel ratio and releases NO_x it has absorbed and reduces the same when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio.
8. An exhaust gas purification device as set forth in claim 1, wherein the purification means comprises both of an NH₃ adsorbing-denitrating catalyst which adsorbs NH₃ in the exhaust gas and reduces NO_x in the exhaust gas using the NH₃ it has adsorbed or the NH₃ in the exhaust gas and an NO_x absorbing-reducing catalyst which absorbs NO_x in the exhaust gas when the exhaust gas is at a lean air-fuel ratio and releases NO_x it has absorbed and reduces the same when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio.
9. An exhaust gas purification device as set forth in claim 8, wherein the NO_x absorbing-reducing catalyst is disposed in the exhaust gas passage upstream of the NH₃ adsorbing-denitrating catalyst.
10. An exhaust gas purification device as set forth in claim 8, wherein the NO_x absorbing-reducing catalyst is disposed in the exhaust gas passage downstream of the NH₃ adsorbing-denitrating catalyst.
11. An exhaust gas purification device as set forth in one of claims 2 through 4, wherein the purification means comprises an NH₃ adsorbing-denitrating catalyst which adsorbs NH₃ in the exhaust gas and reduces NO_x in the exhaust gas using the NH₃ it has adsorbed or the NH₃ in the exhaust gas and wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH₃ produced by the NH₃ conversion means in accordance with the amount of NO_x emitted from the engine.
12. An exhaust gas purification device as set forth in claim 5, wherein the purification means comprises an NH₃ adsorbing-denitrating catalyst which adsorbs NH₃ in the exhaust gas and reduces NO_x in the exhaust gas using the NH₃ it has adsorbed or the NH₃ in the exhaust gas and wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH₃ produced by the NH₃ conversion means in accordance with the amount of NO_x emitted from the engine.
13. An exhaust gas purification device as set forth in one of claims 2 through 4, wherein the purification means comprises an NO_x absorbing-reducing catalyst which absorbs NO_x in the exhaust gas when the exhaust gas is at a lean air-fuel ratio and releases NO_x it has absorbed and reduces the same when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio and wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH₃ produced by the NH₃ conversion means in accordance with the amount of NO_x emitted from the engine.
14. An exhaust gas purification device as set forth in claim 5, wherein the purification means comprises an NO_x absorbing-reducing catalyst which absorbs NO_x in the exhaust gas when the exhaust gas is at a lean air-fuel ratio and releases NO_x it has absorbed and reduces the same when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio and wherein the exhaust gas air-fuel ratio adjusting means controls the amount of NH₃ produced by the NH₃ conversion means in accordance with the amount of NO_x emitted from the engine.
15. An exhaust gas purification device as set forth in claim 1, wherein the purification means comprises an NH₃ adsorbing-denitrating catalyst which adsorbs NH₃ in the exhaust gas and reduces NO_x in the exhaust gas using the NH₃ it has adsorbed or the NH₃ in the exhaust gas and wherein the exhaust gas air-fuel ratio adjusting means adjusts the exhaust gas at a rich air-fuel ratio when the amount of the NH₃ adsorbed in the NH₃ adsorbing-denitrating catalyst becomes smaller than a predetermined value.

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16. An exhaust gas purification device as set forth in claim 1, wherein the purification means comprises an NO_x absorbing-reducing catalyst which absorbs NO_x in the exhaust gas when the exhaust gas is at a lean air-fuel ratio and releases NO_x it has absorbed and reduces the same when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio and wherein the exhaust gas air-fuel ratio adjusting means adjusts the exhaust gas at a rich air-fuel ratio when the amount of the NO_x absorbed in the NO_x absorbing-reducing catalyst becomes larger than a predetermined value.

17. An exhaust gas purification device as set forth in claim 1, wherein the NH₃ conversion means comprises a three-way reducing and oxidizing catalyst.

18. An exhaust gas purification device as set forth in claim 1, wherein the NH₃ conversion means comprises an NO_x absorbing-reducing catalyst which absorbs NO_x in the exhaust gas when the exhaust gas is at a lean air-fuel ratio and releases NO_x it has absorbed and reduces the same when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio.

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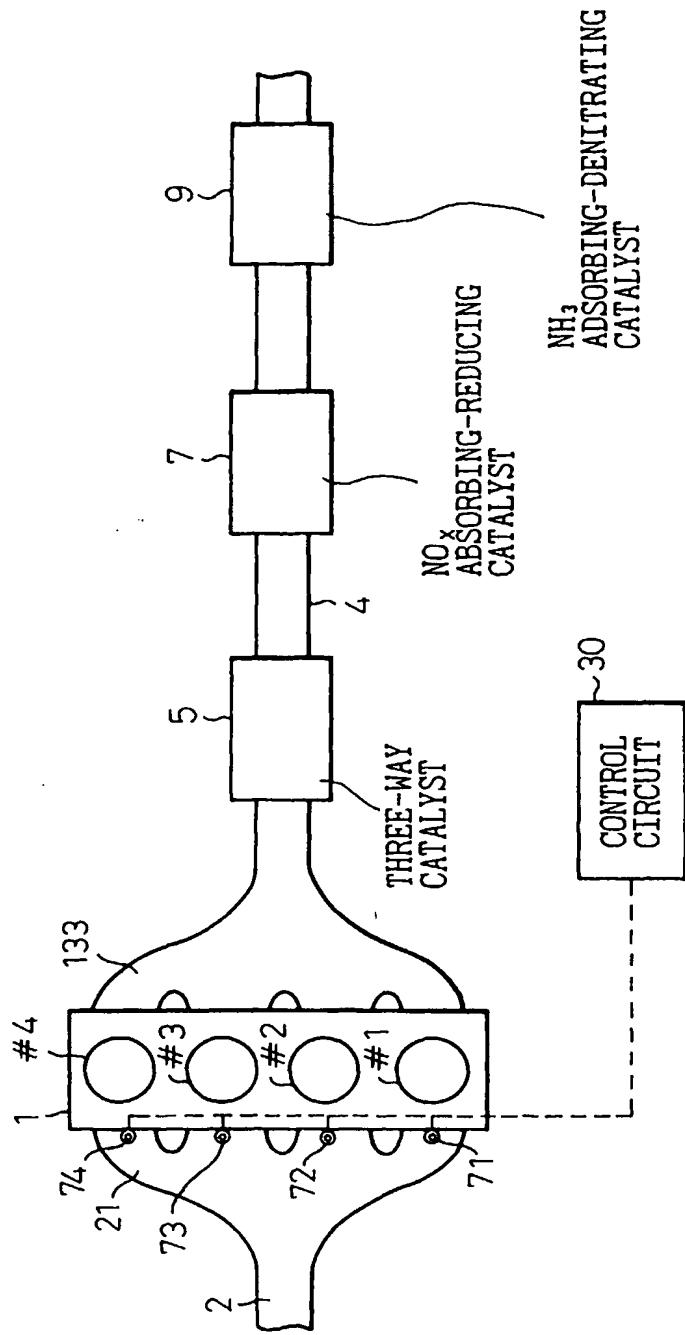
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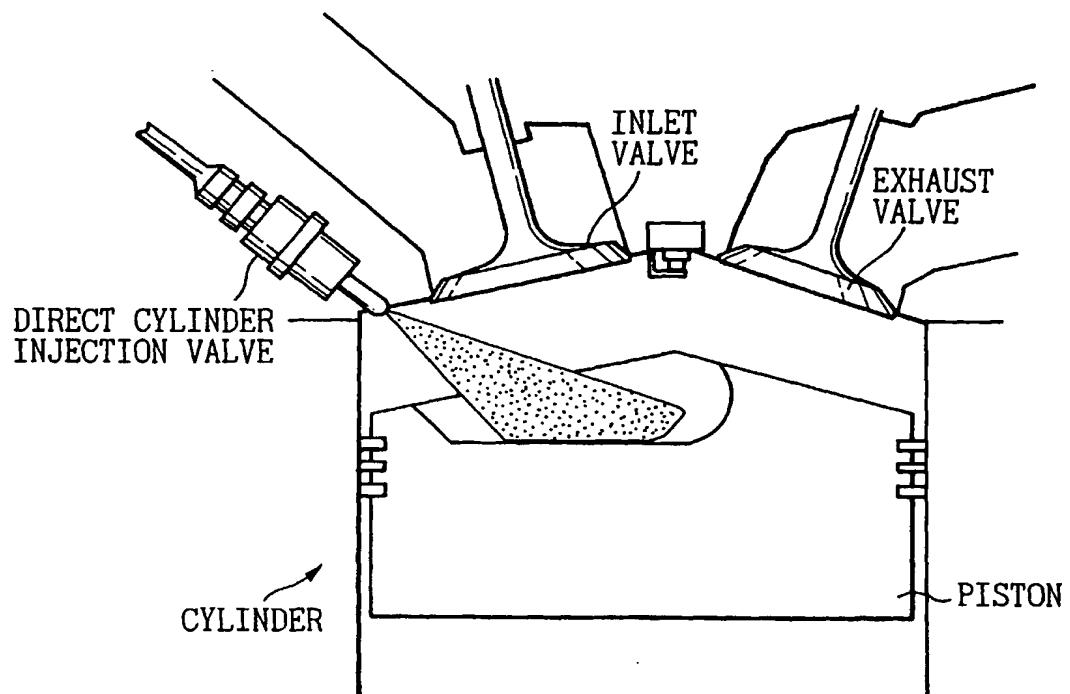
EP 0 878 609 A2

Fig. 1



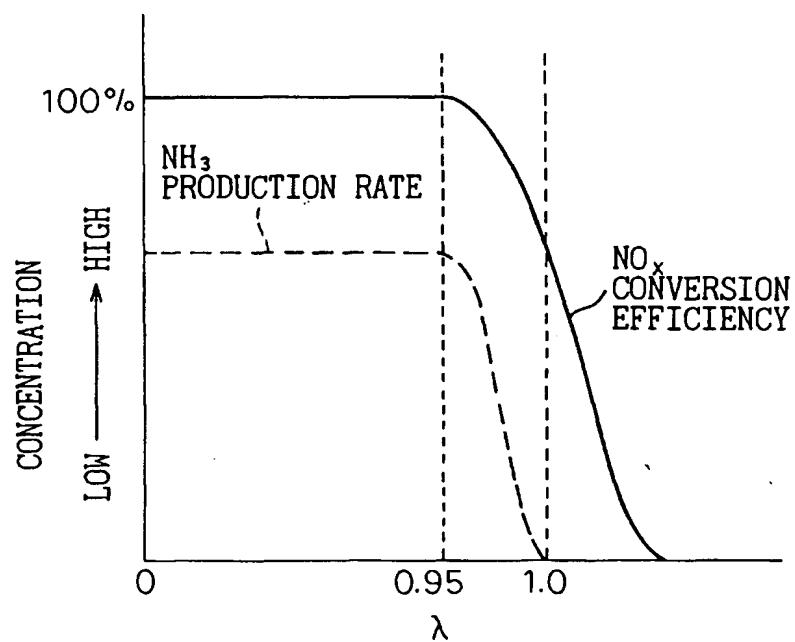
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Fig. 2



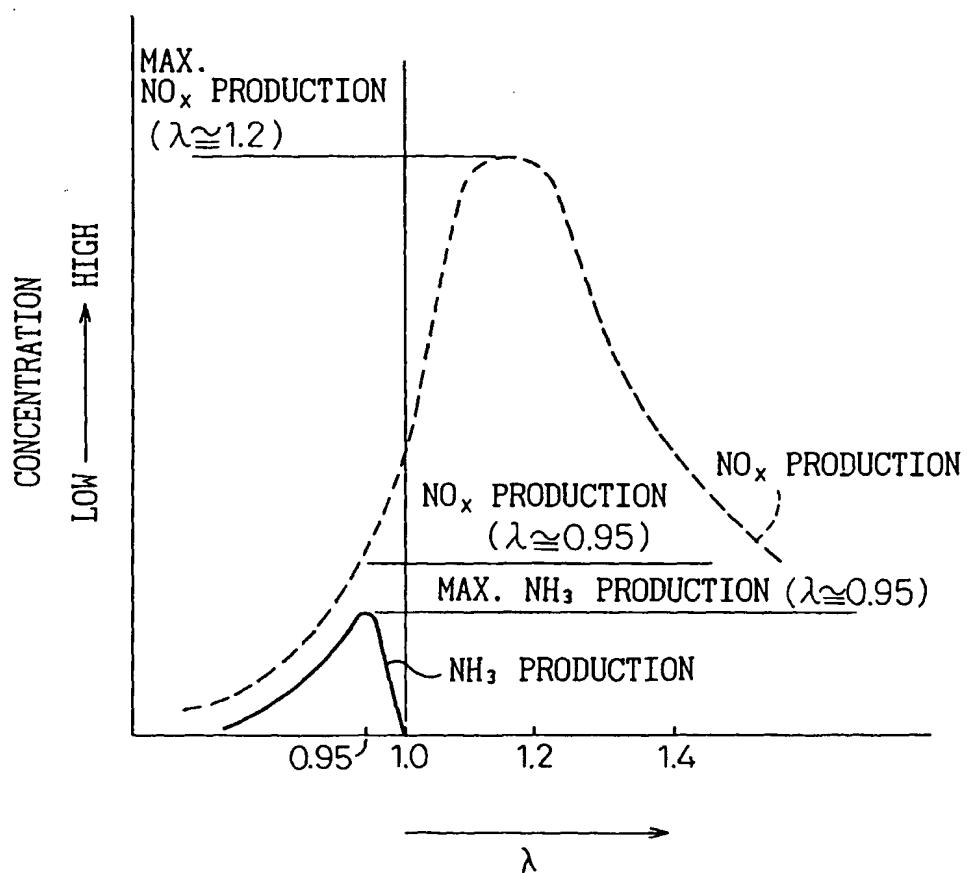
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Fig. 3



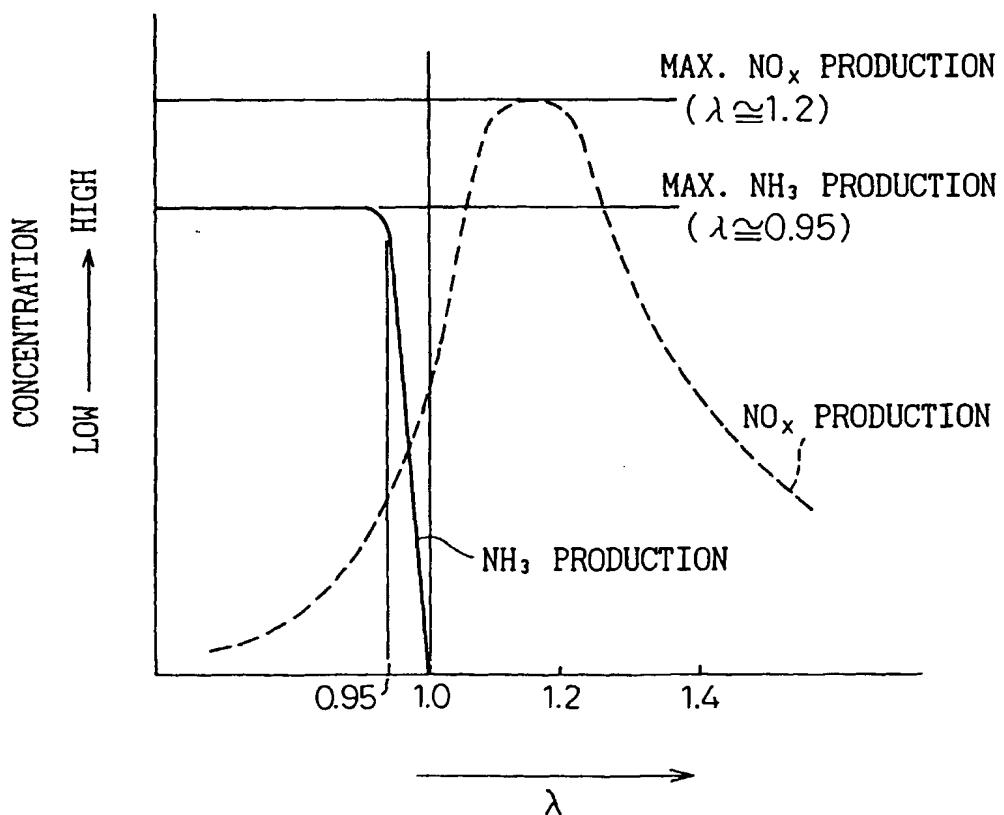
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Fig. 4
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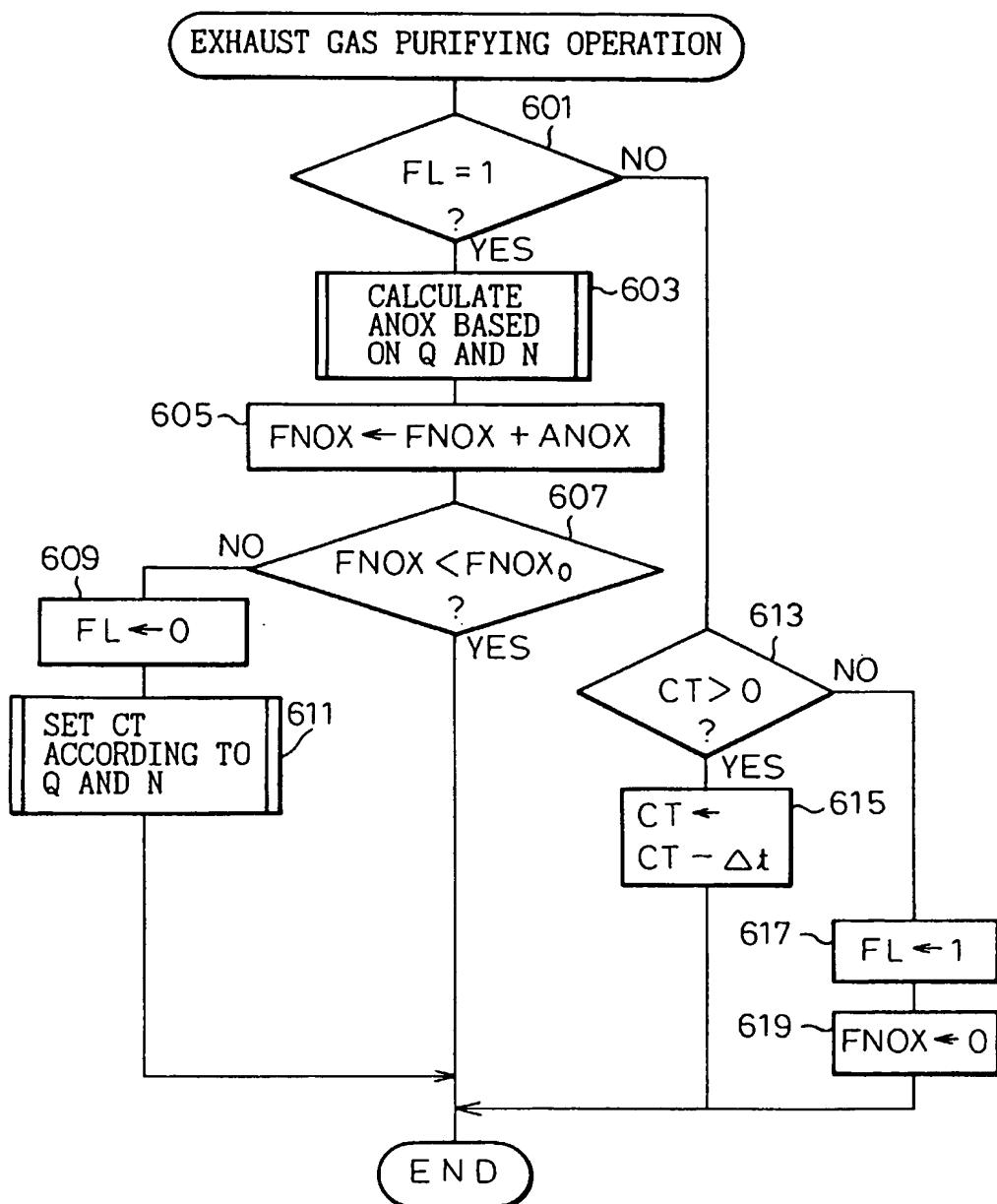
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Fig.5



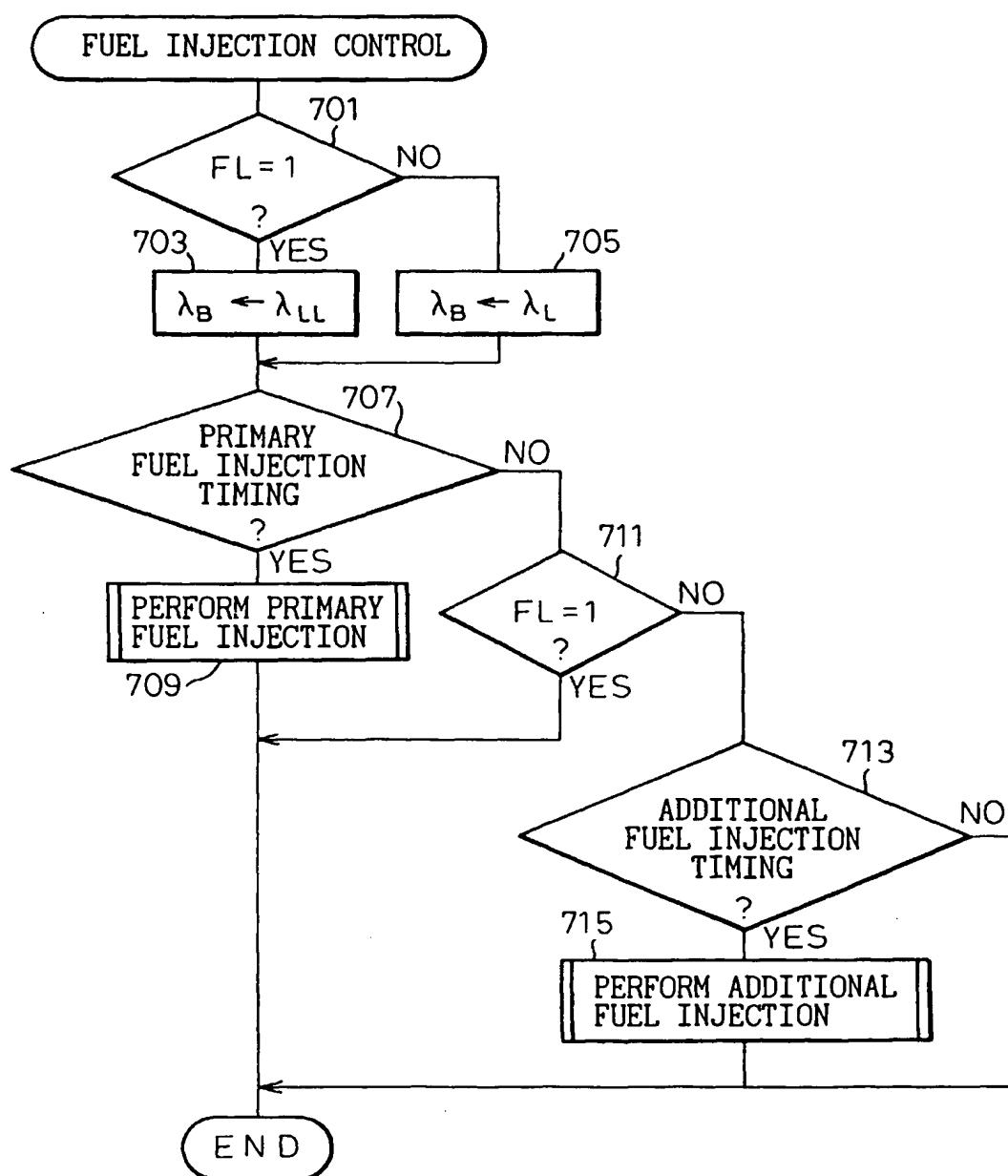
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Fig.6



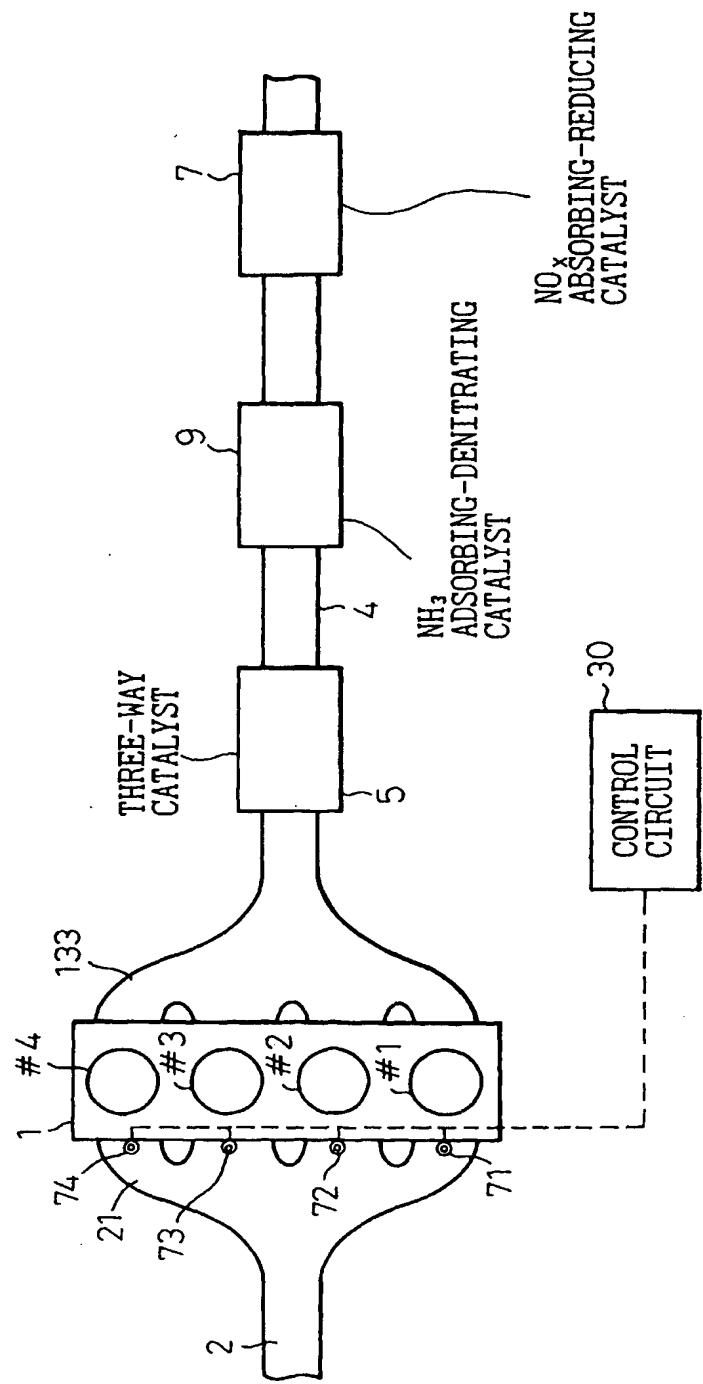
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Fig.7



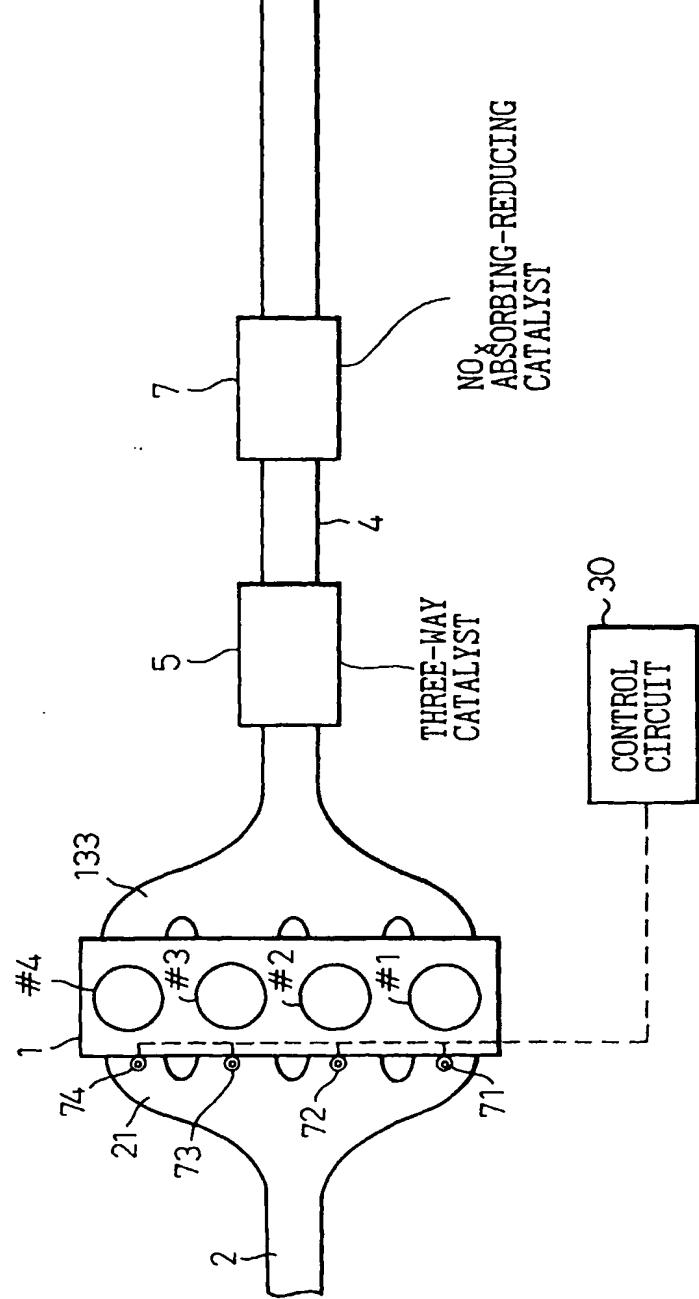
EP 0 878 609 A2

Fig. 8



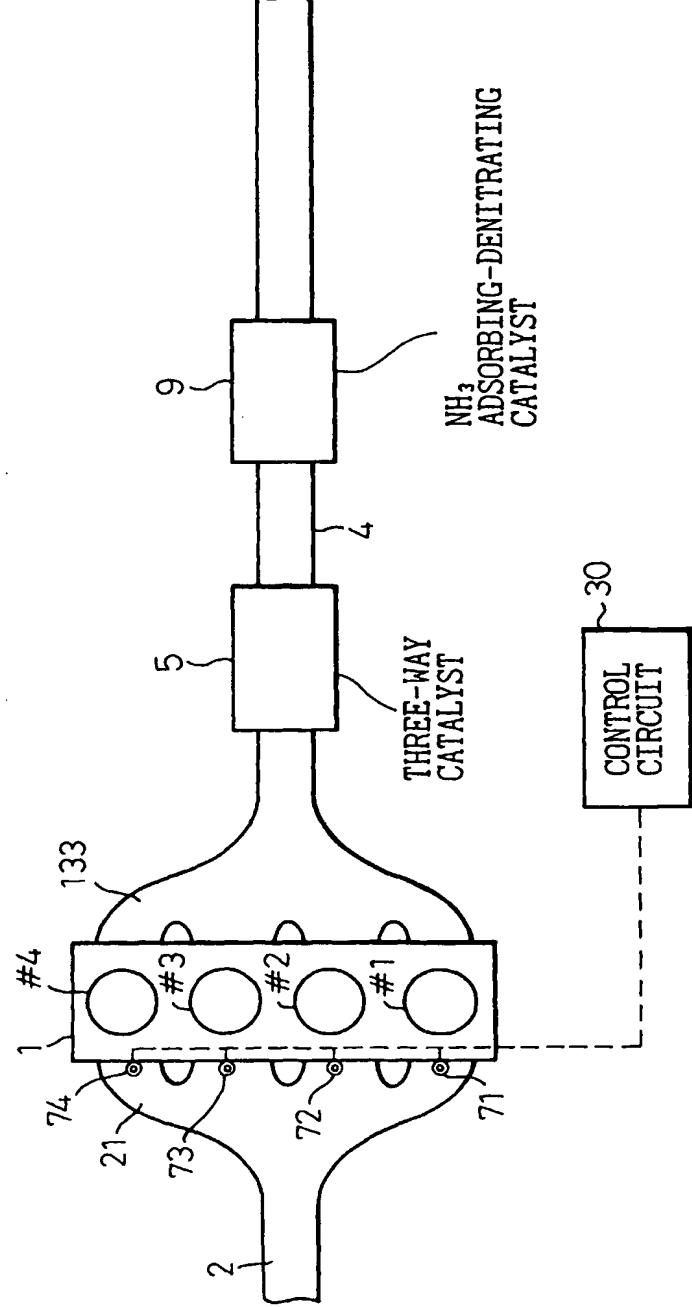
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Fig. 9



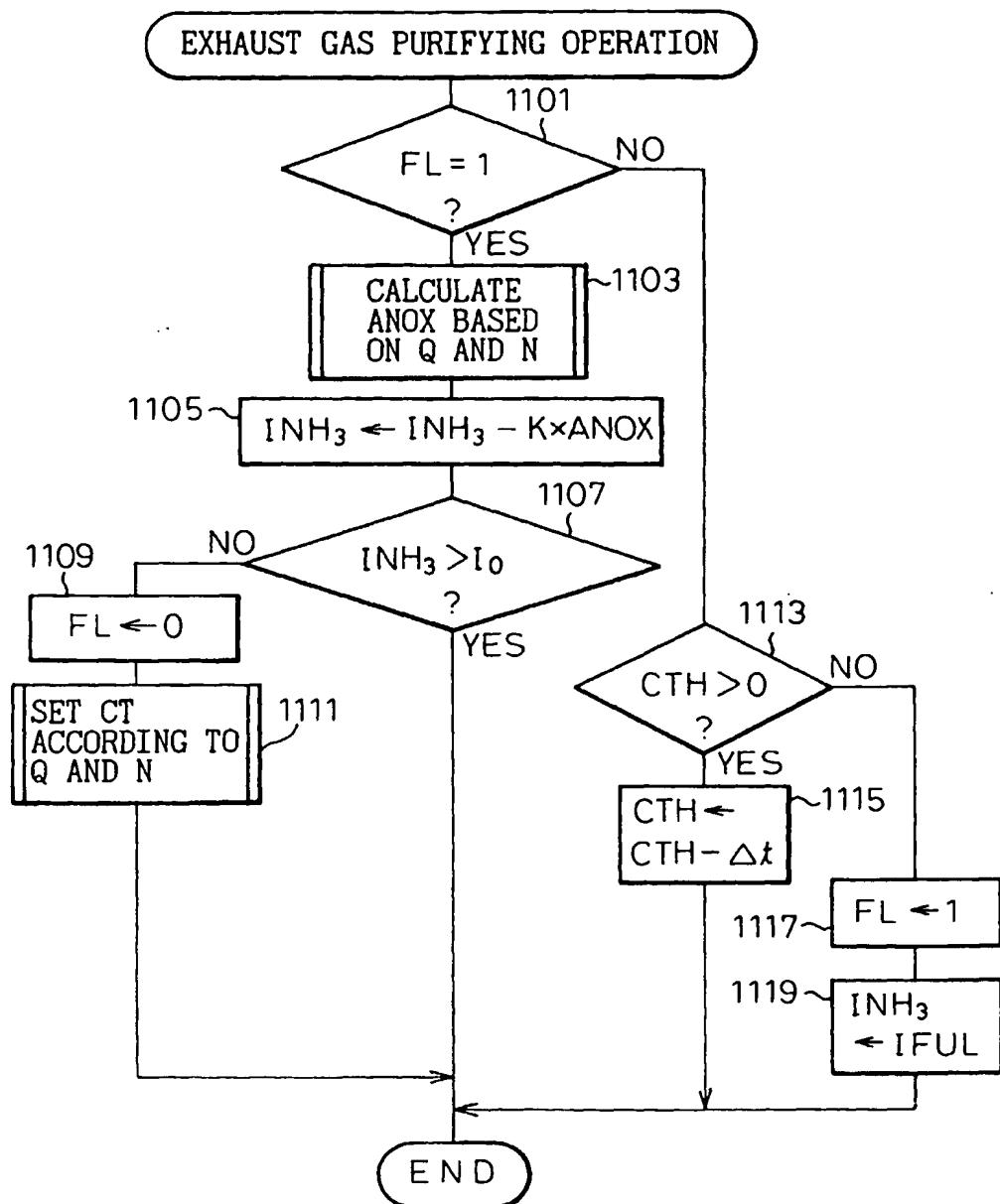
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Fig.10



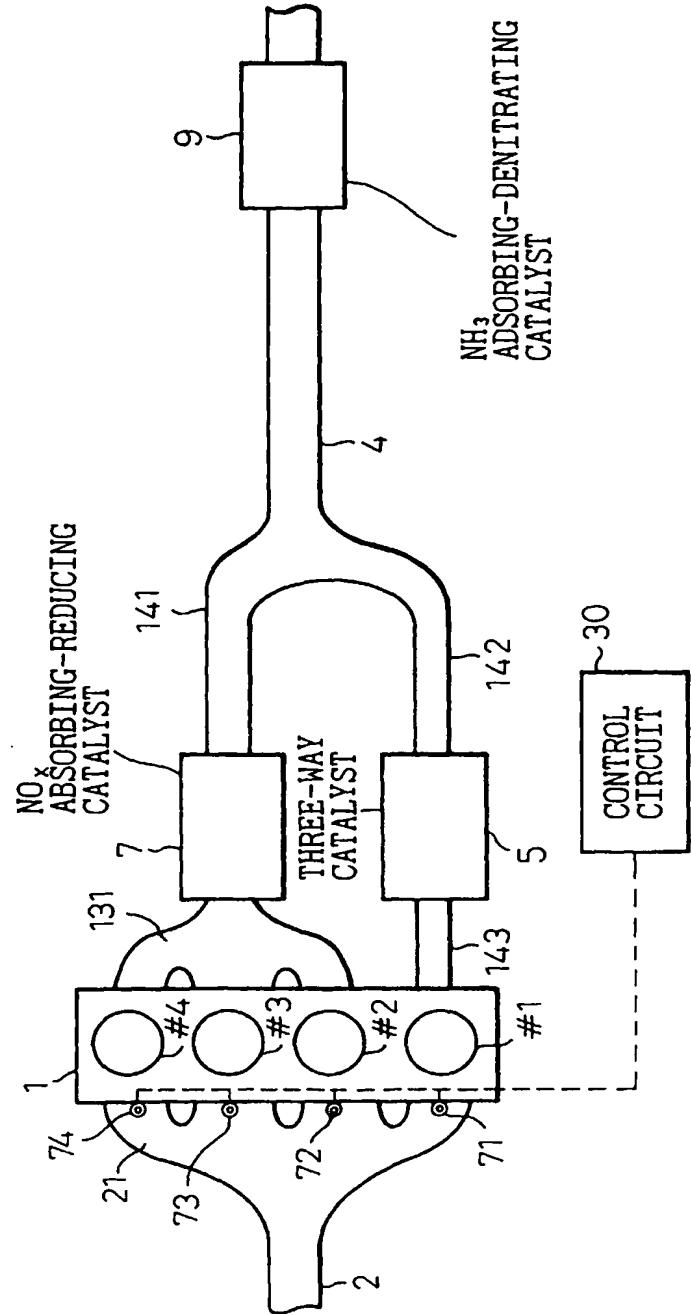
EP 0 878 609 A2

Fig.11



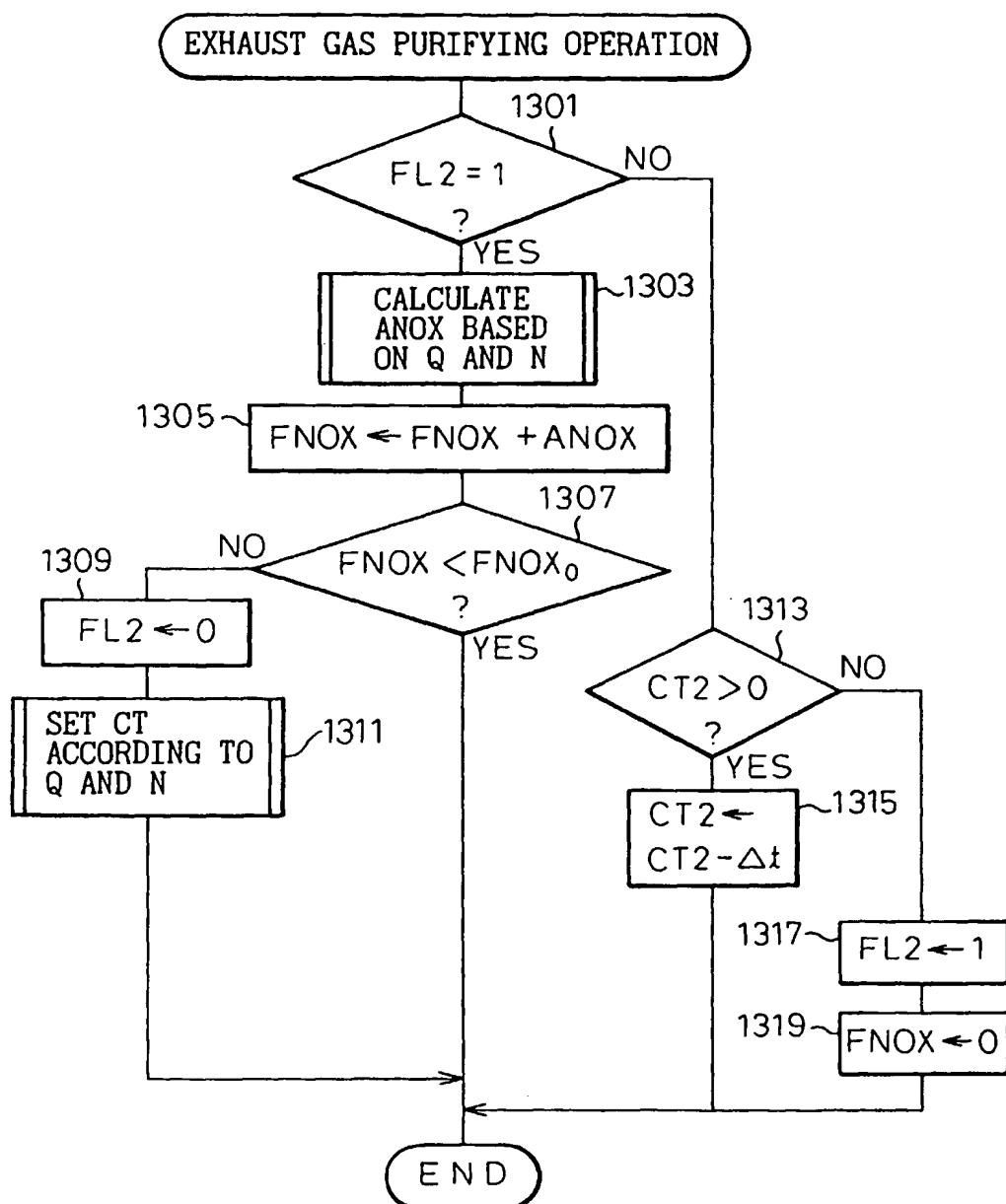
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Fig. 12



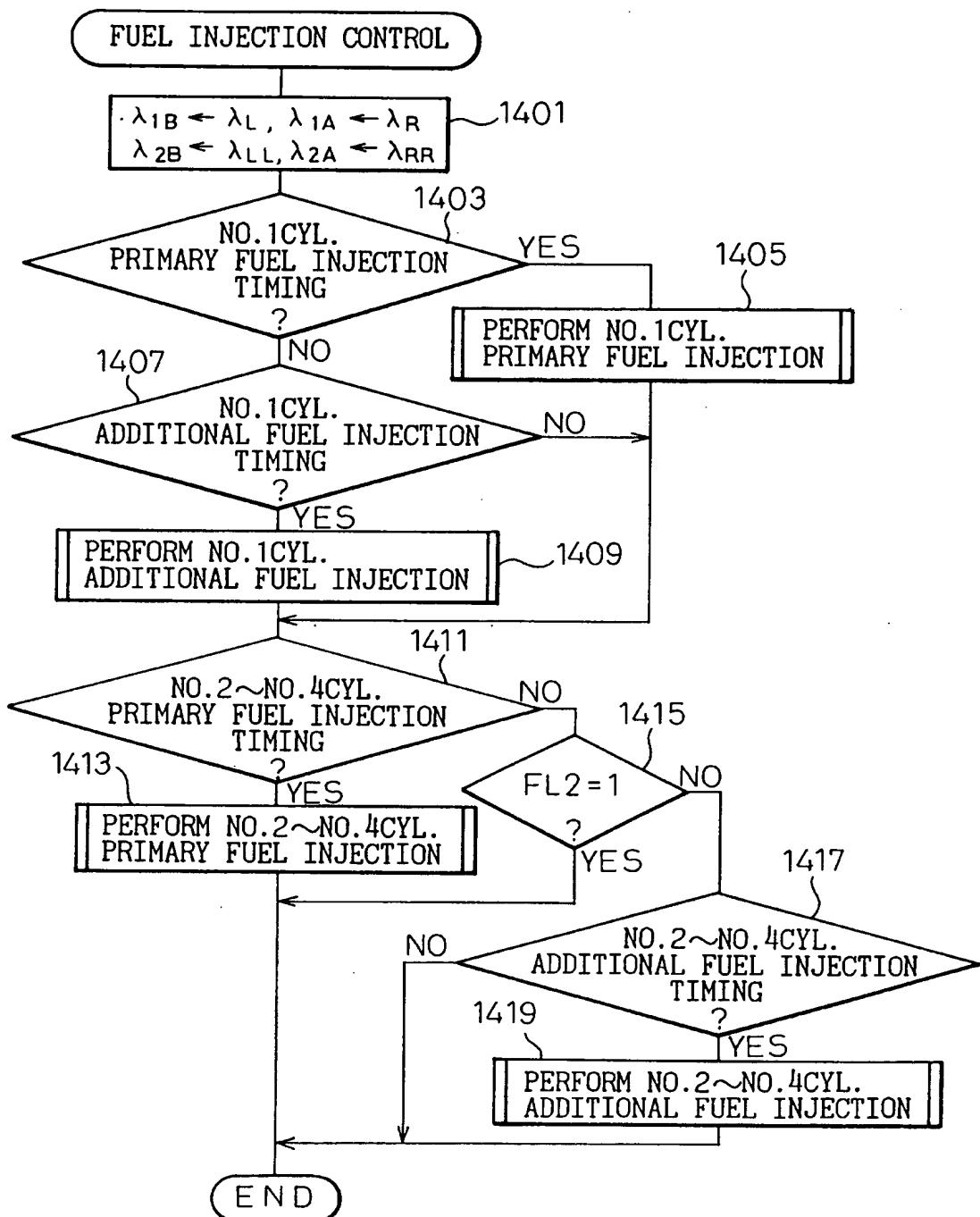
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Fig.13



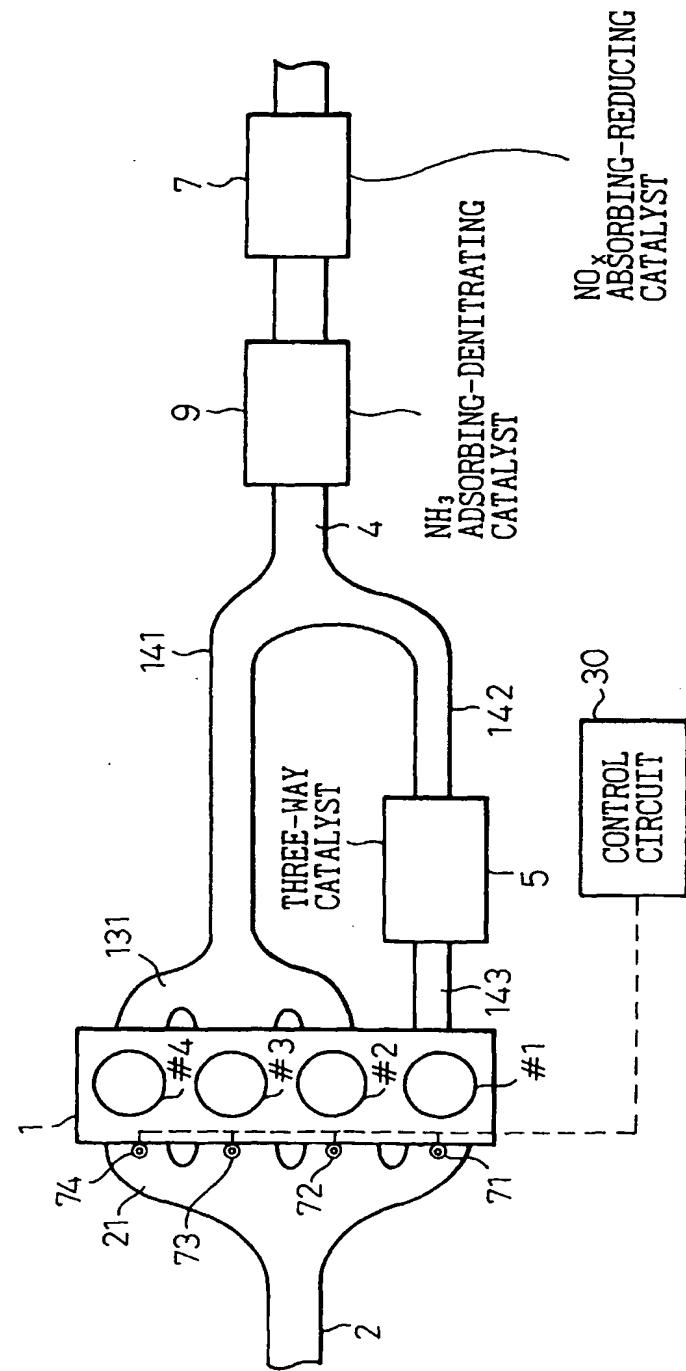
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Fig.14



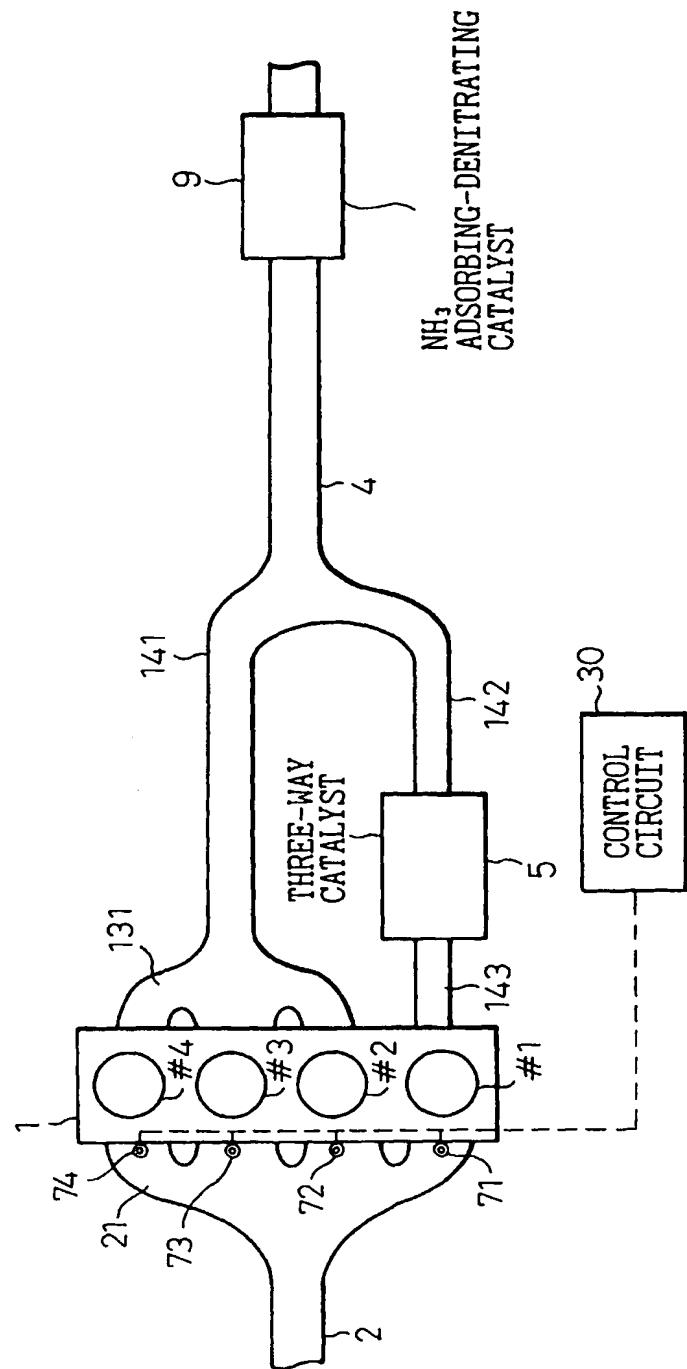
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Fig.15



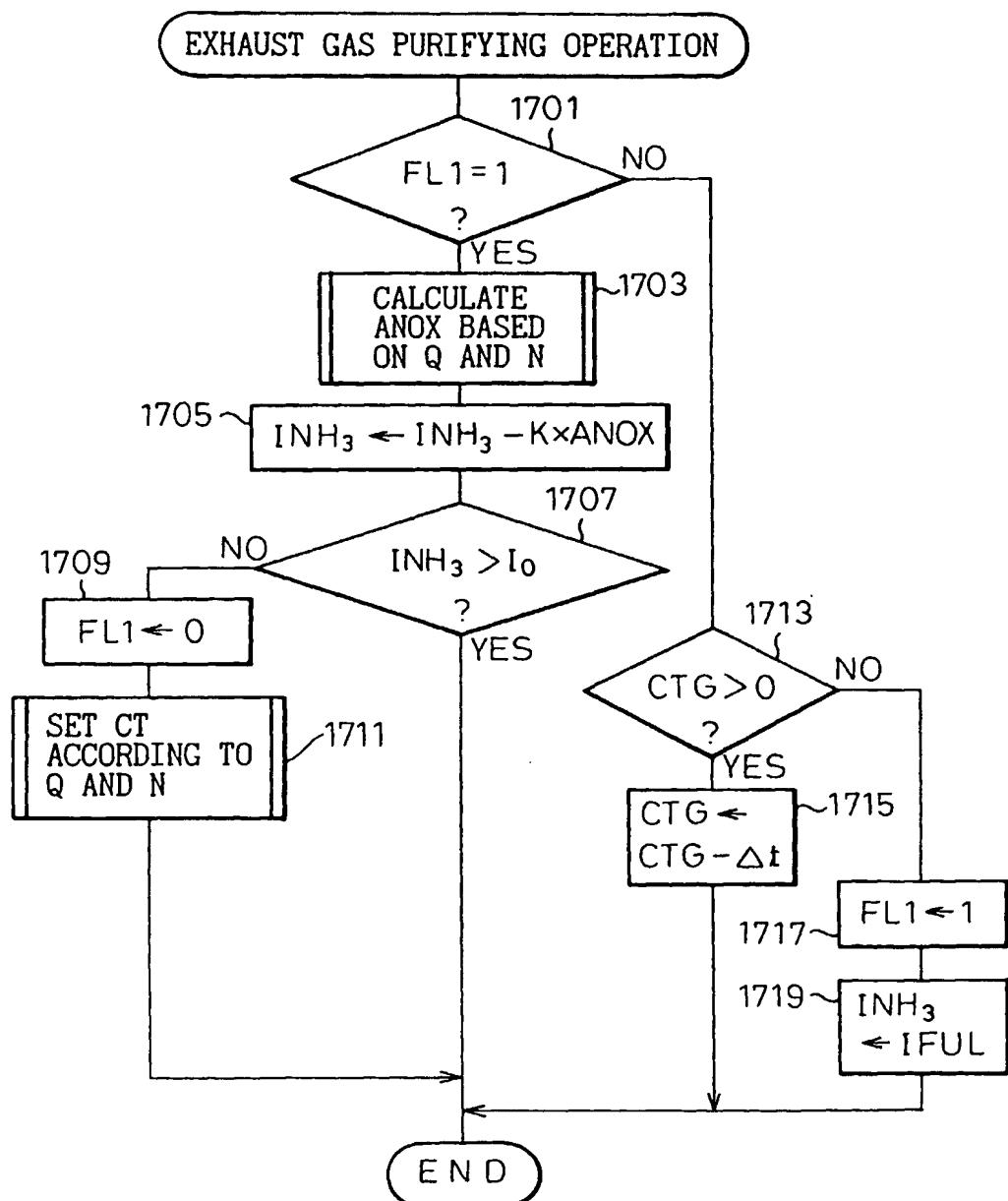
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Fig. 16



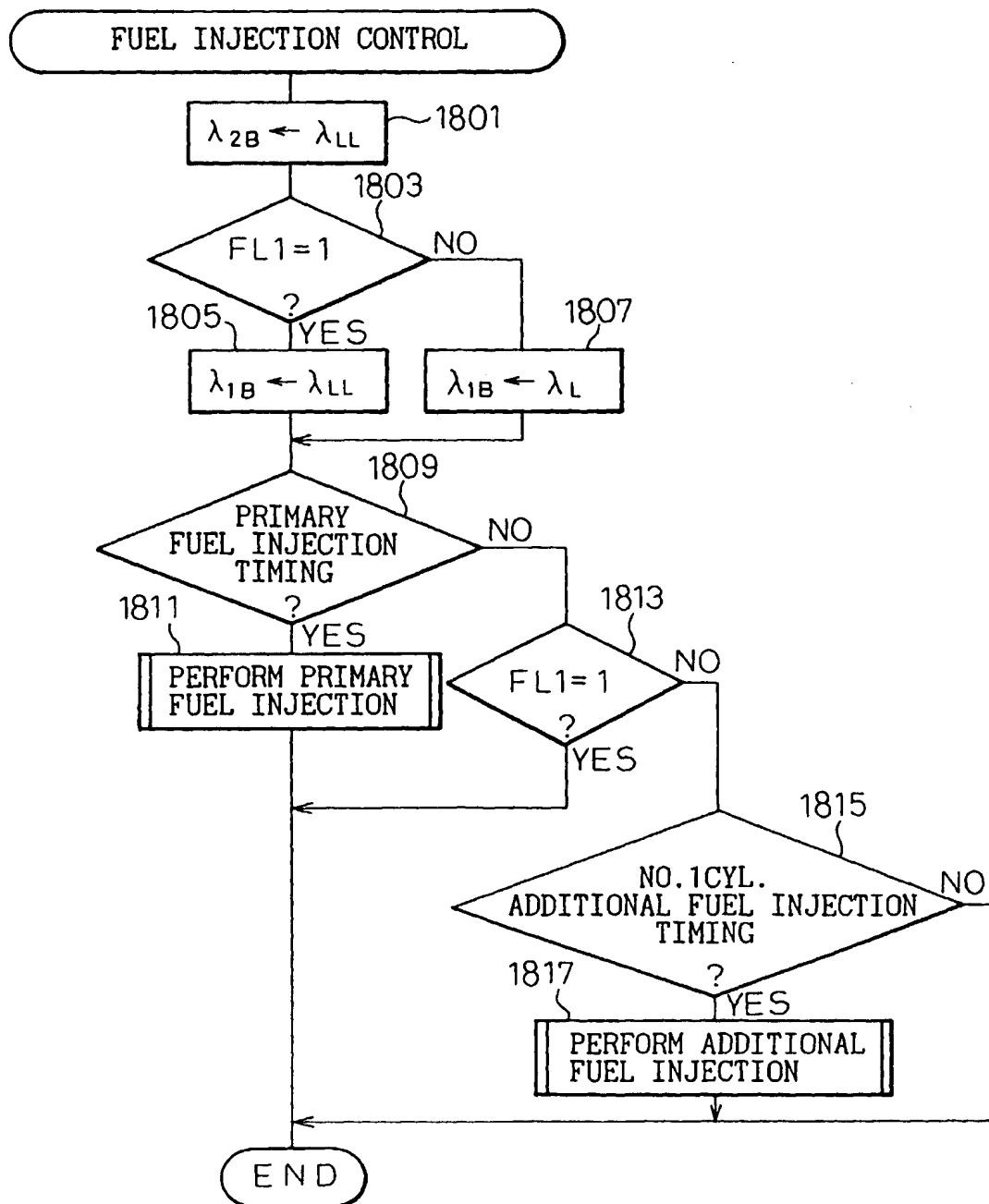
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Fig.17



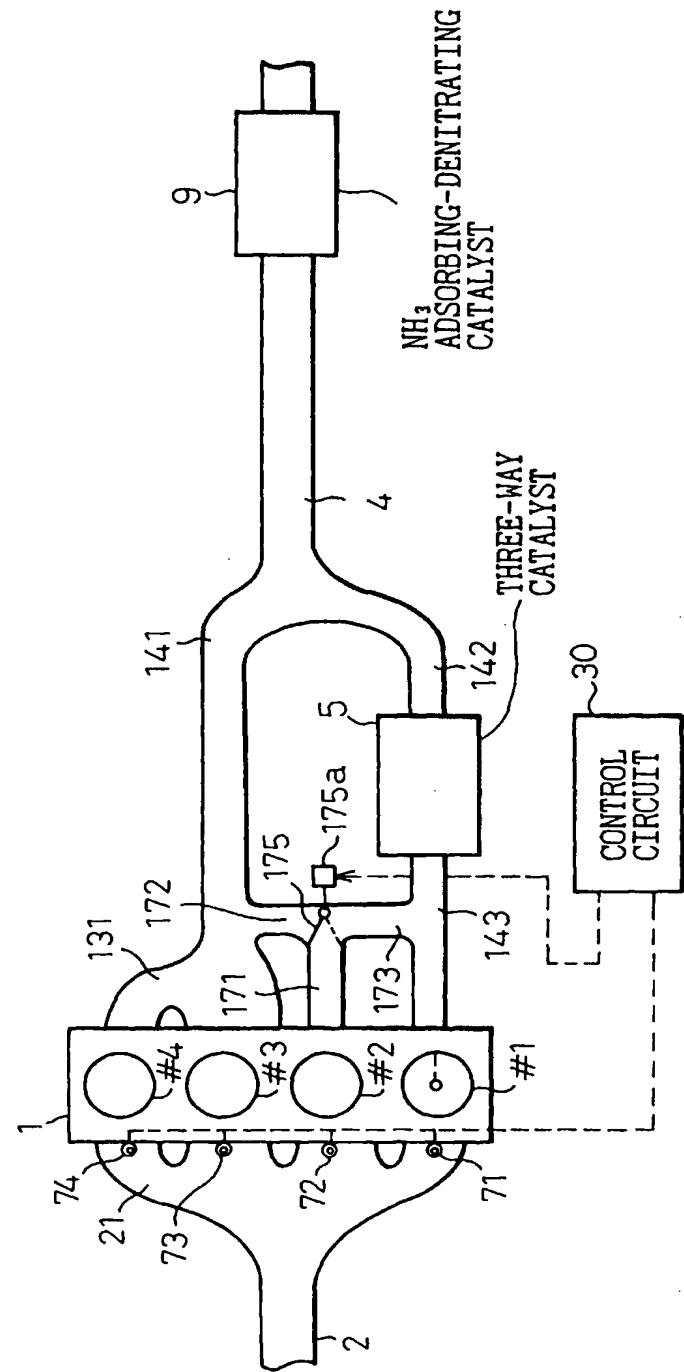
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Fig.18



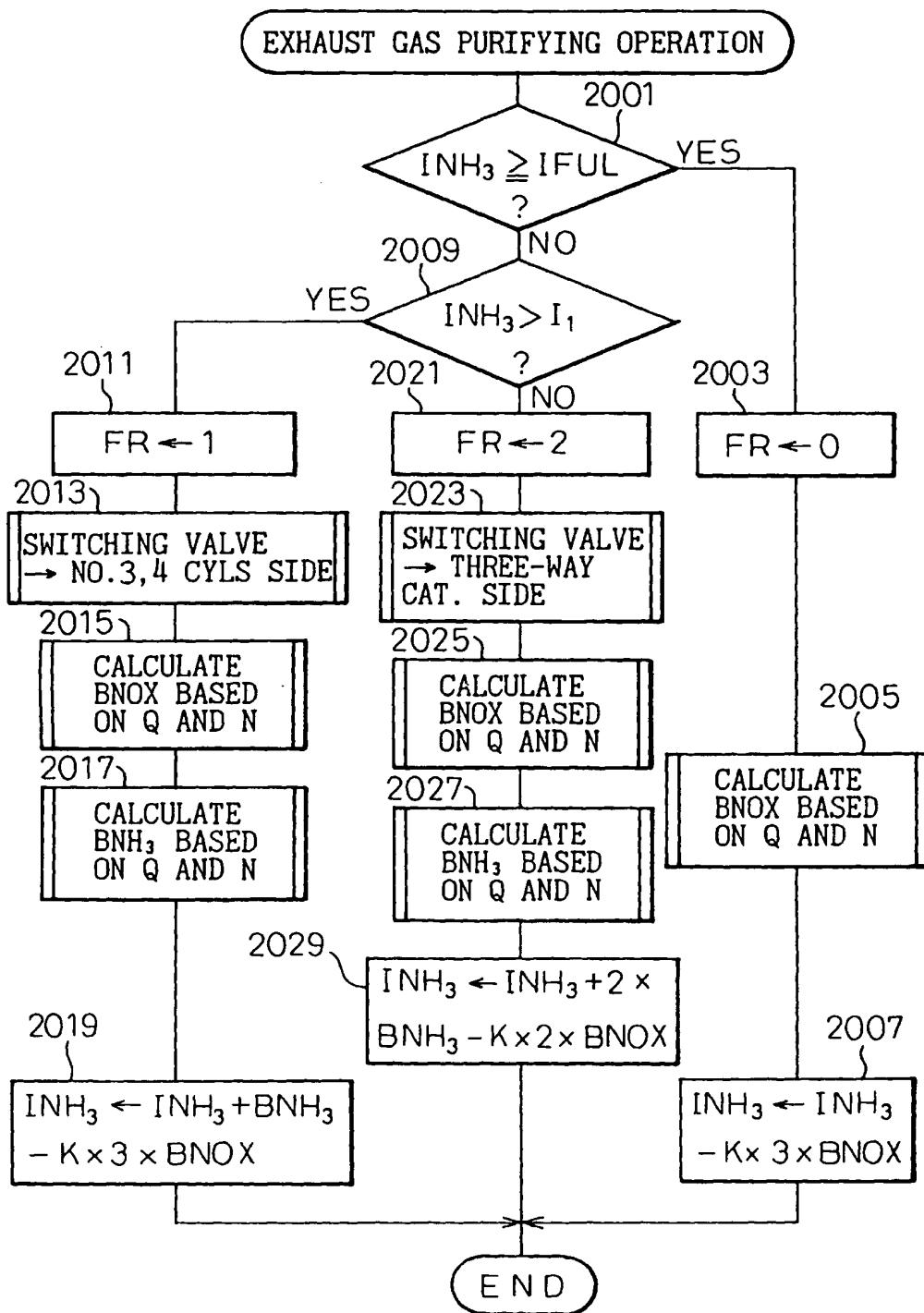
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Fig. 19



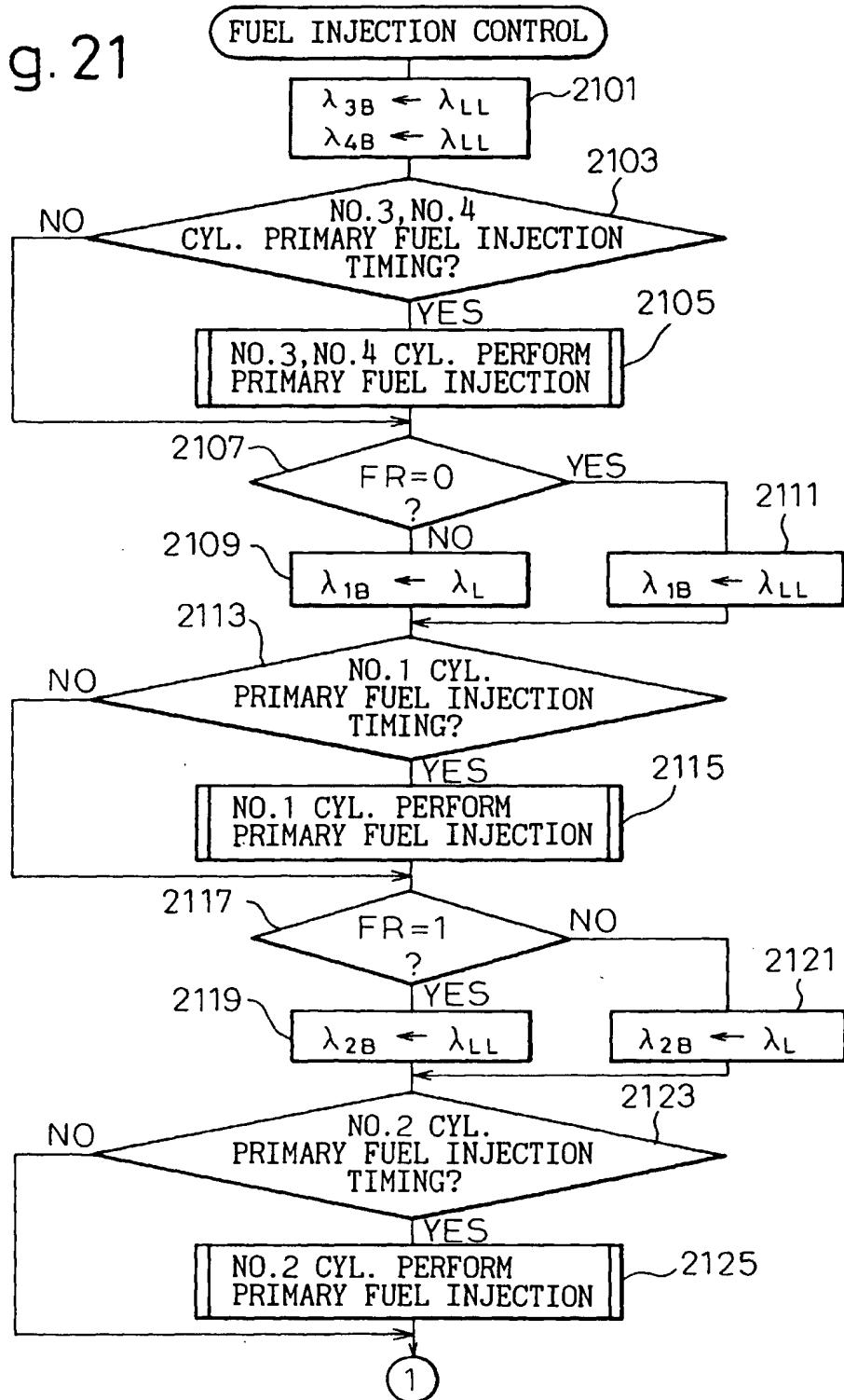
EP 0 878 609 A2

Fig. 20



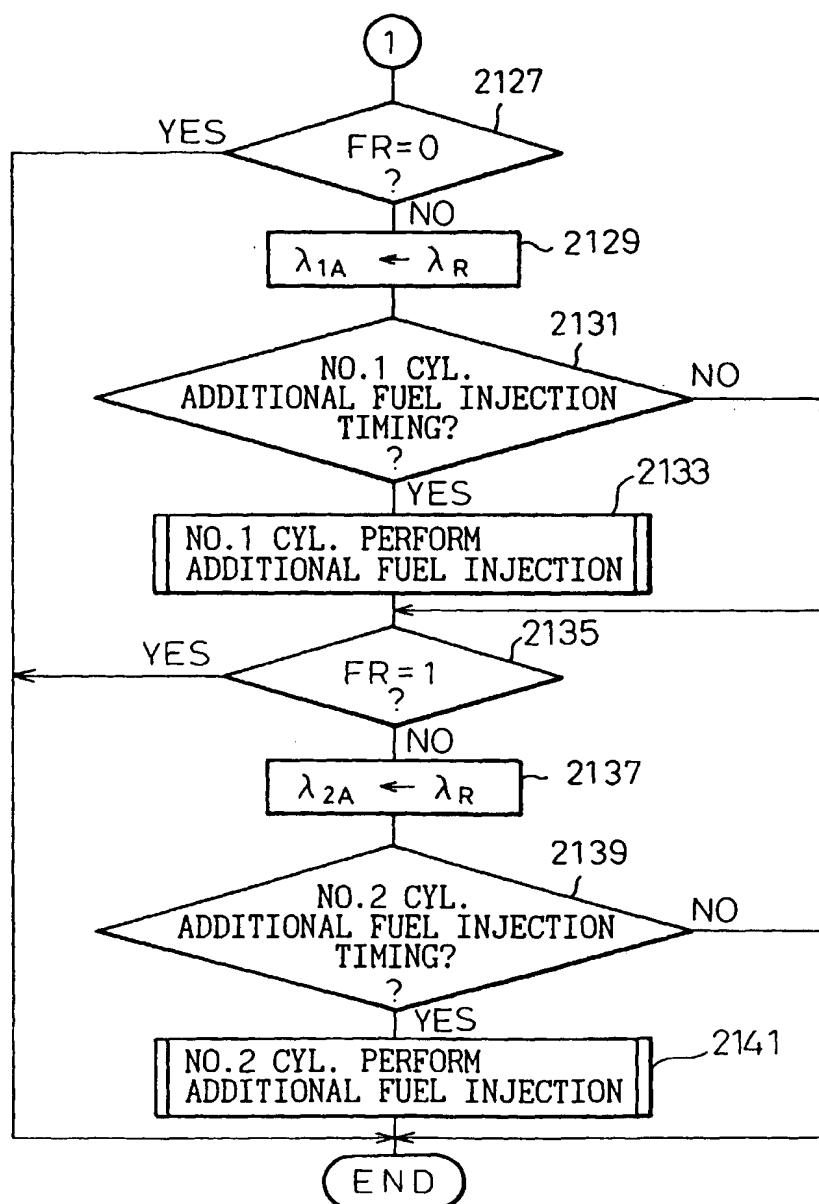
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Fig. 21



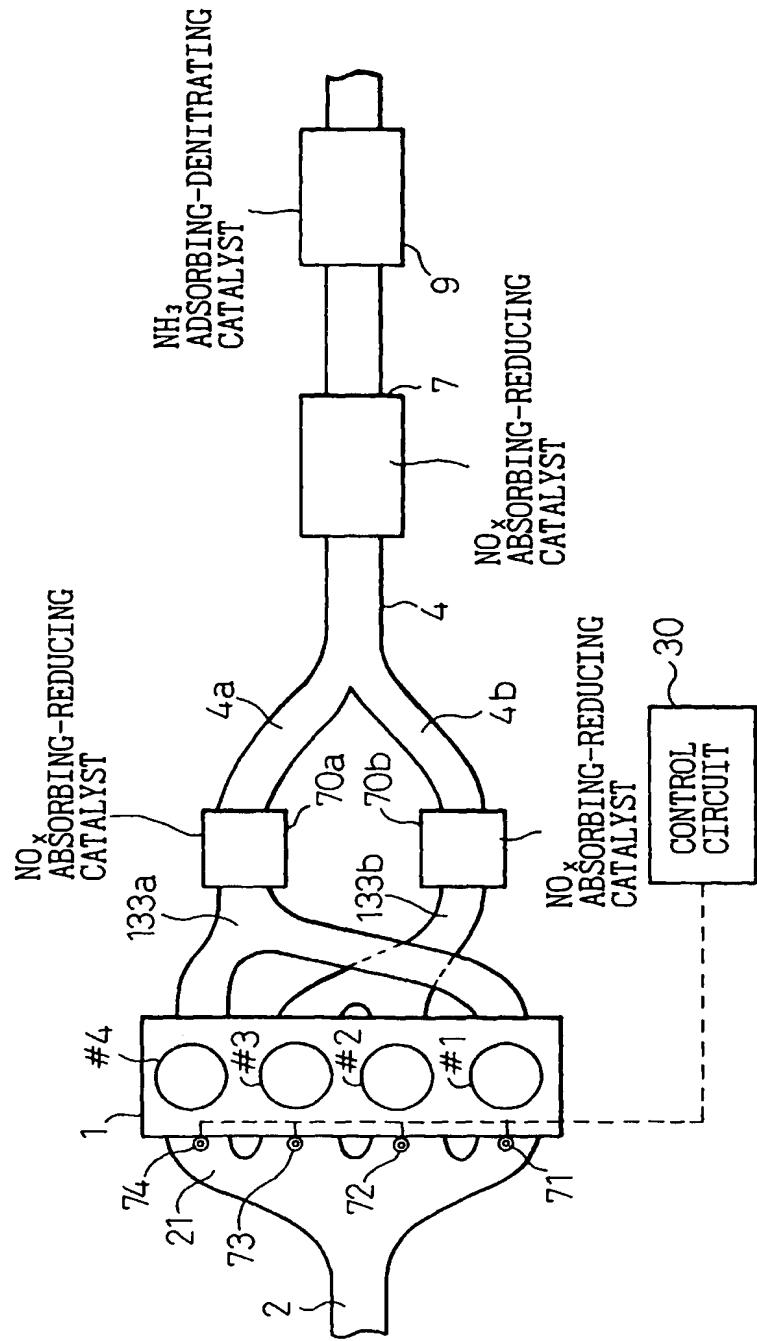
EP 0 878 609 A2

Fig.22



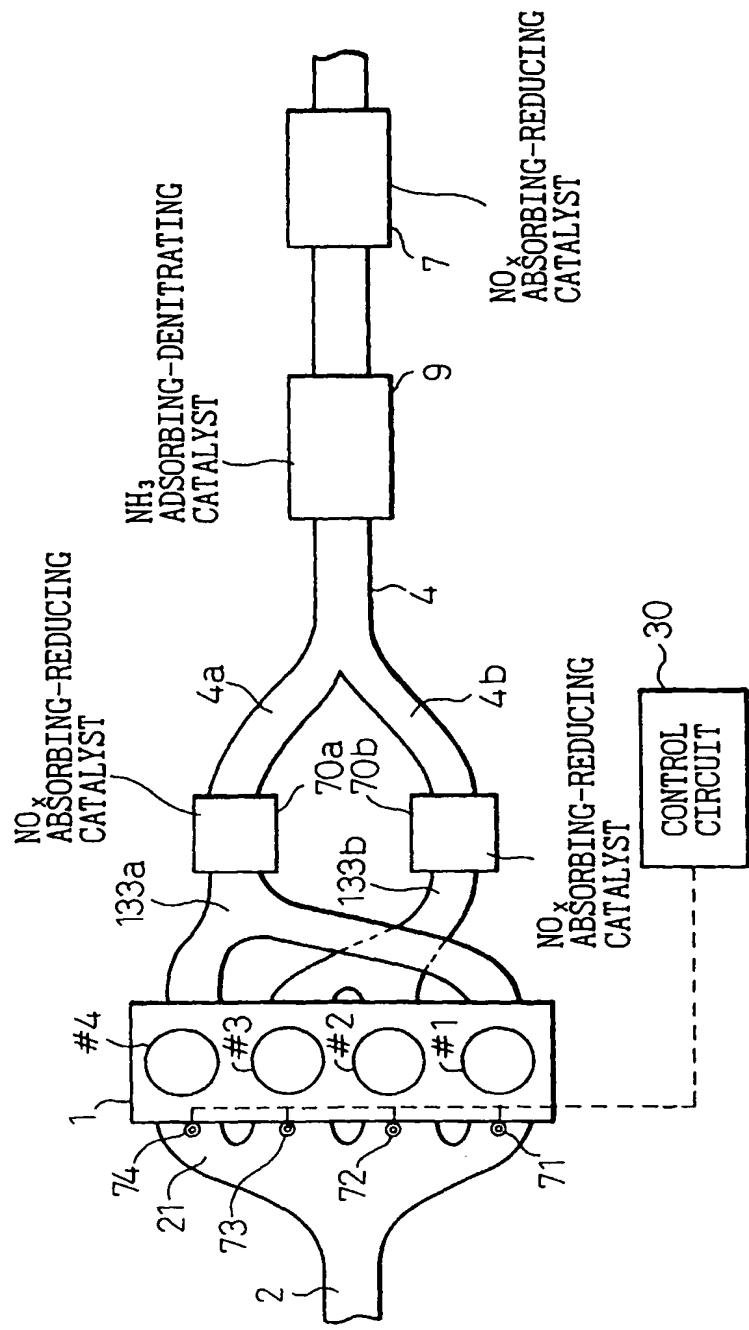
EP 0 878 609 A2

Fig. 23



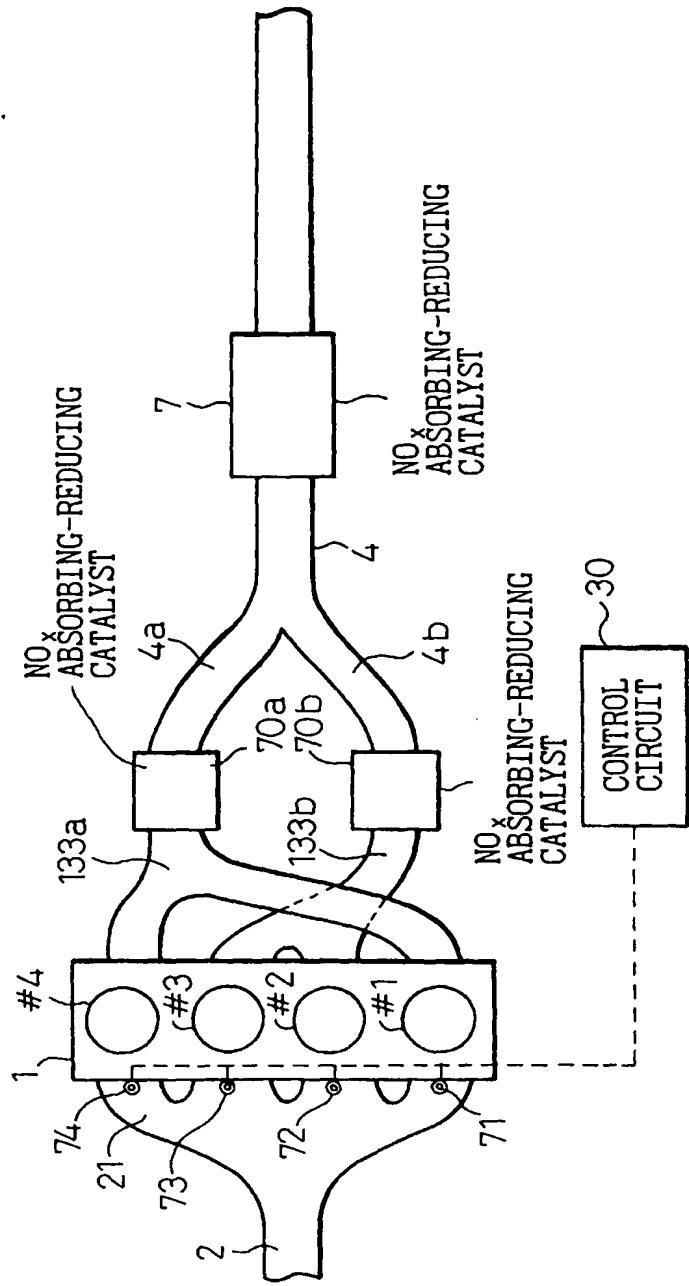
EP 0 878 609 A2

Fig. 24



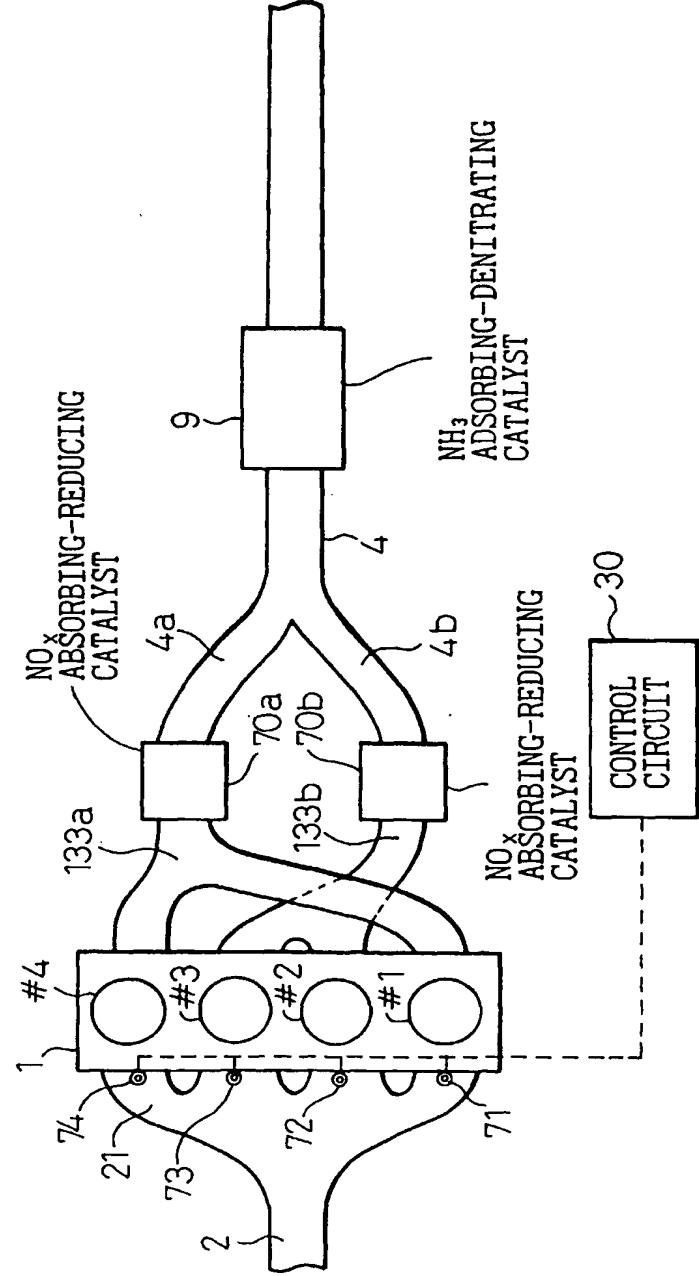
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Fig. 25



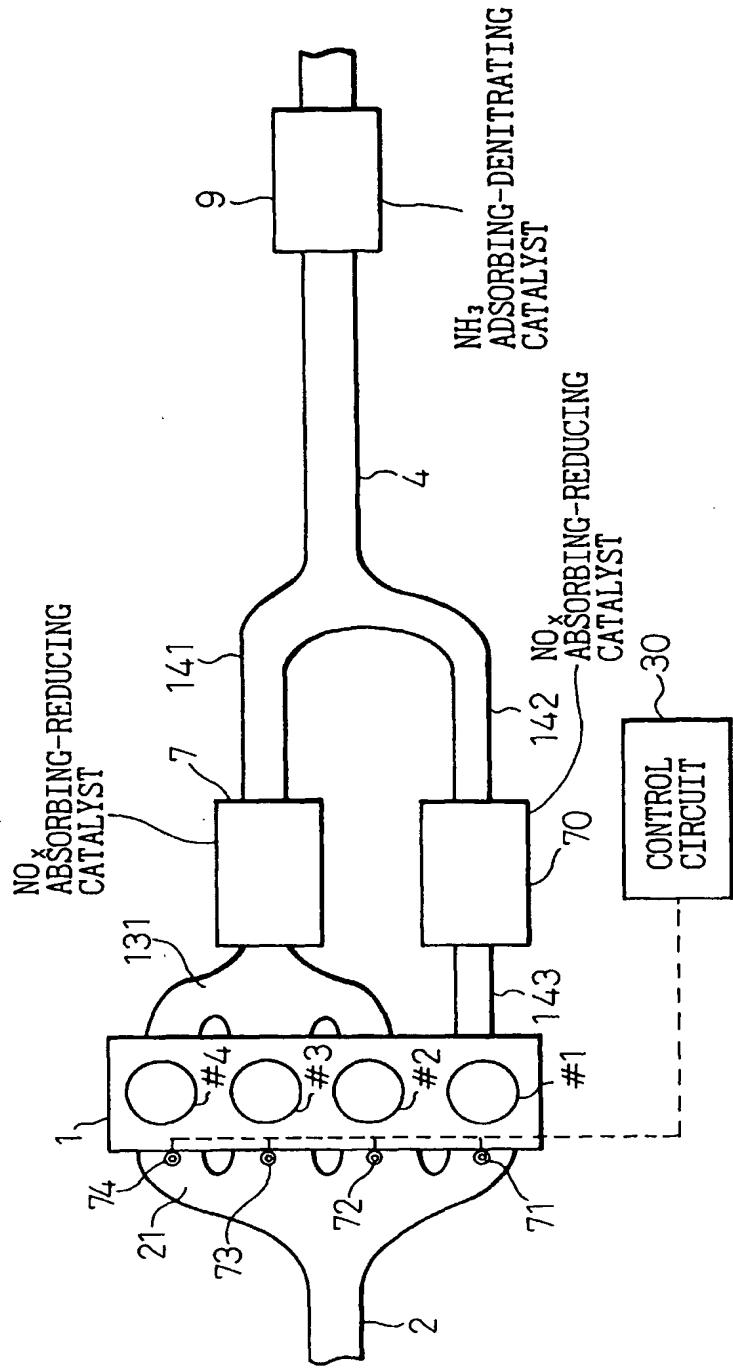
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Fig. 26



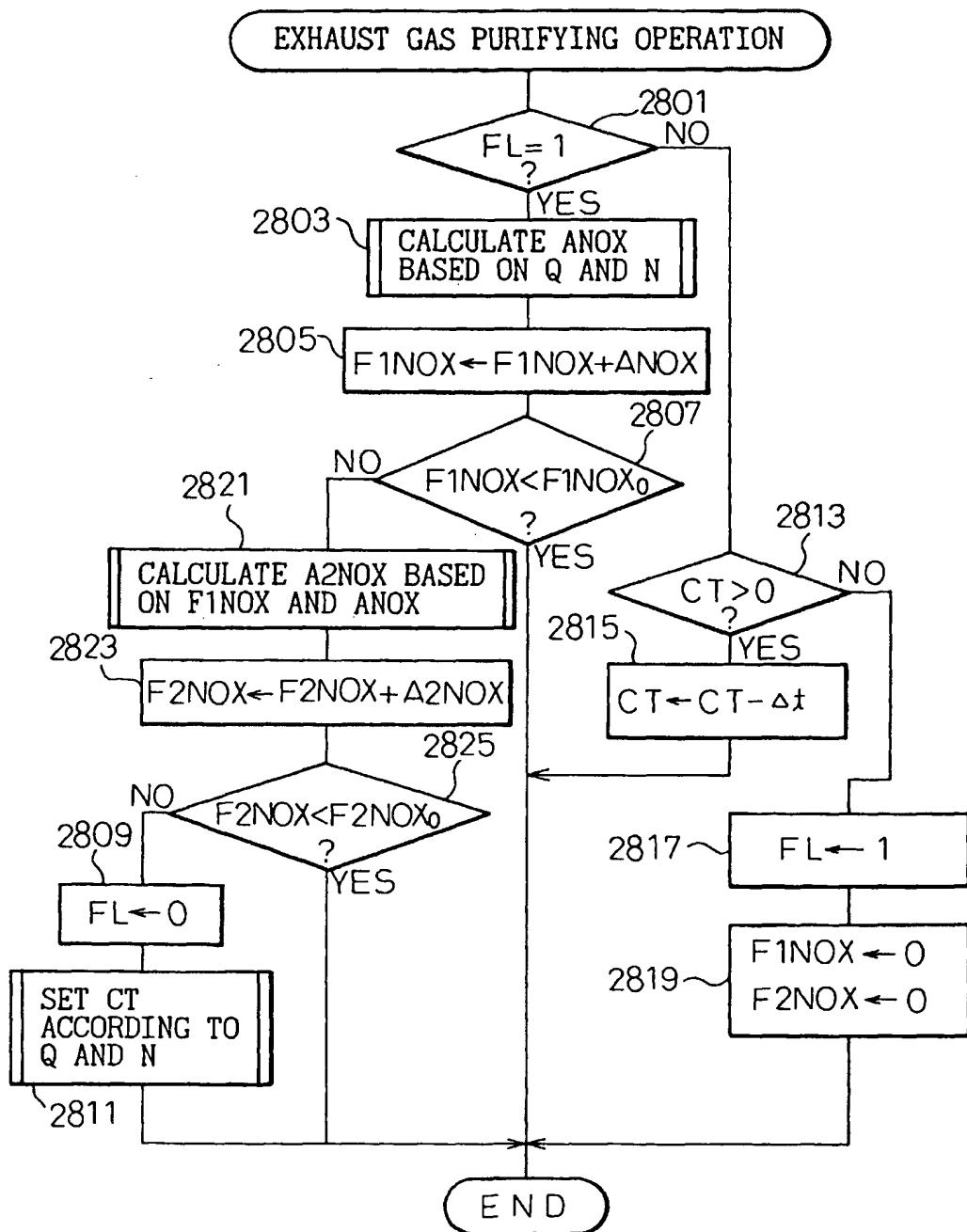
EP 0 878 609 A2

Fig. 27



EP 0 878 609 A2

Fig.28



EP 0 878 609 A2

Fig. 29

